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LXXVI.—ON THE BEHAVIOR OF ACYLTHIONCARBAMIC ESTERS WITH ALKYL IODIDES AND AMINES: BENZOYLIMIDOTHIOCARBONIC ESTERS, ACYCLIC BENZOYLPSEUDOUREAS AND BENZOYLUREAS.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

In this paper we describe the results of an examination of some acetyl and benzoyl thioncarbamic esters as regards their behavior with alkyl iodides and with organic bases. This examination led us to the investigation of a series of benzoylimidothiocarbonic esters, $C_6H_5CO—N=C\begin{matrix}SR\\OR\end{matrix}$, acylpseudourea ethers, $C_6H_5CO—N=C\begin{matrix}NRR'\\OR\end{matrix}$, and benzoylureas, $C_6H_5CONHCONRR'$, a preliminary account of which is also given.

The acylthioncarbamic esters are prepared by the union of acyl rhodanides with alcohols:

$$RCO—NCS + HOCH_3 = RCO—NHCS.OCH_3.^1$$

We find that these compounds have little tendency to undergo molecular rearrangement with alkyl iodides, a fact which is probably due to the negative character of the molecules. We observed that a rearrangement took place only in the case of the acetyl and benzoyl methyl esters when warmed, within narrow limits, with methyl iodide:

$$\underset{\text{I.}}{CH_3CO—NHCS.OCH_3} \rightarrow \underset{\text{II.}}{CH_3CONHCO.SCH_3}.$$

The same thiol compound (II) was obtained by warming methyl thiolcarbamate, $H_2NCO.SCH_3$, with acetic anhydride on the water-bath, in the same way that Andreocci[2] found that xanthogenamide may be acetylated, this being the best method for the preparation of the acetylthioncarbamic esters.

These results show that the compounds formed by the union of acyl rhodanides with alcohols have the thion structure, I, which was assigned to them by Miquel[3] and Dixon,[4] and not the thiol structure as represented, subject to interrogation, in Beilstein's "Handbuch."[5]

We find that methyl benzoylthioncarbamate reacts more readily with chloracetic acid than with alkyl iodides, giving benzoylcarbaminthioglycollic acid:

$$C_6H_5CONHCS.OCH_3 \rightarrow C_6H_5CONHCO.SCH_2CO_2H.$$

In previous papers it has been shown that such thioncarbamic esters as have a more or less positive nature,[6] especially the phenylthioncarbazinic esters,

$$C_6H_5NH—NHCS.OC_2H_5,^7$$

readily react with alkyl halides and with compounds of a negative character; while, on the other hand, with organic bases they proved to be quite inert.

We now find in the case of the negative benzoylthioncarbamic esters, $C_6H_5CO.NHCS.OR$, that the behavior is pre-

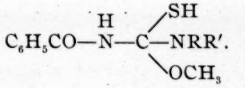
[1] Miquel: Ann. chim. phys., 1877 [5], **11**, 318.
[2] Ber. d. chem. Ges., **25**, R. 640.
[3] *Loc. cit.*
[4] J. Chem. Soc. (London), 1899, 378.
[5] Dritte Auflage, II, p. 1181.
[6] Wheeler and Barnes: This JOURNAL, **22**, 141.
[7] *Ibid.*

cisely the reverse. These compounds react with ammonia and organic bases at ordinary temperatures, but the course of the reaction is not what might, perhaps, be expected, since a smooth direct replacement, as represented by the following equation, does not take place :

$$C_6H_5CONHCS.OCH_3 + HNRR' =$$
$$C_6H_5CONHCSNRR' + CH_3OH.$$

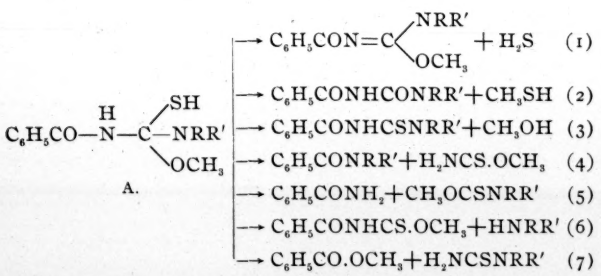
We find, instead of this, that the benzoylthioncarbamic esters unite with 1 molecule of a primary or secondary organic base, giving addition-products, which, we believe, are best represented by the general formula A.

$$C_6H_5CO{-}NHCS.OCH_3 + HNRR' =$$



A.

The crude addition-products in most cases appear to be oils or varnishes which decompose more or less readily. We have isolated two examples of these, however, and in one case the product is a solid. An addition-product, as represented here, might be expected to decompose, on warming or on standing, in at least seven different ways, giving the following compounds or their decomposition-products :



A.

(1) $C_6H_5CON{=}C(NRR')(OCH_3) + H_2S$

(2) $C_6H_5CONHCONRR' + CH_3SH$

(3) $C_6H_5CONHCSNRR' + CH_3OH$

(4) $C_6H_5CONRR' + H_2NCS.OCH_3$

(5) $C_6H_5CONH_2 + CH_3OCSNRR'$

(6) $C_6H_5CONHCS.OCH_3 + HNRR'$

(7) $C_6H_5CO.OCH_3 + H_2NCSNRR'$

As a matter of fact we have obtained examples of the first six of these modes of decomposition. The ease and manner

in which the addition-products decompose depend mostly on the character of the amine radicals R and R′, and it may be stated that the above decompositions probably do not all take place in a single experiment. Generally, only two or three of them occur simultaneously. The most widely observed are represented by reactions (1) and (2), while of 13 amines which were allowed to act on benzoylmethyl and ethylthioncarbamic esters, reaction (3) was found to take place in quantity in only one instance.

For example, alcoholic ammonia reacts with ethyl benzoylthioncarbamate almost quantitatively according to (1). The aryl amines, aniline, toluidine, xylidine, α-naphthylamine, etc., and also benzylamine, react mostly according to (1) and to a less extent as represented by (2). A considerable evolution of hydrogen sulphide takes place (1), while mercaptan (2) is also noticed, and the corresponding benzoylarylureas are easily isolated in a state of purity. The presence of benzoylpseudourea ethers (1) was established as shown below.

Diisobutylamine reacts with methyl benzoylthioncarbamate according to (1), (2), (3), and (4). On heating a mixture of these substances, which in the cold forms a varnish, hydrogen sulphide, mercaptan, and alcohol were evolved. The presence of benzoylpseudomethyldiisobutylurea, $C_6H_5CO—N=C\begin{matrix}N(C_4H_9)_2\\OCH_3\end{matrix}$, was established and benzoyldiisobutylthiourea and diisobutylbenzamide were isolated.

Ethyl acetylthioncarbamate reacts with aniline, on warming, mostly according to (4), and β-naphthylamine was observed to behave in a similar manner with the benzoylmethyl ester.

Diisoamylamine unites with methyl benzoylthioncarbamate giving an example of the addition-product A, which is a solid at ordinary temperatures. The ester and amine combine, when mixed in molecular proportions, with evolution of heat, but no gas is given off until the addition-product is heated to about 80°, the decomposition then proceeding chiefly according to (5) and (1). Hydrogen sulphide is evolved and benzamide (5) and diamylamine are obtained as the chief

products of the reaction. The same products are obtained when hydrogen sulphide is passed into benzoylpseudomethyldiisoamylurea, $C_6H_5CO—N=C\begin{matrix}N(C_5H_{11})_2\\OCH_3\end{matrix}$, at 60°. The fact that the pseudourea ether is not obtained here, at least not as the chief product, is therefore explained. The presence of diisoamylthiourethane was looked for but it was not found. When this addition-product is allowed to stand over sulphuric acid a slow decomposition or dissociation according to (6) takes place.

The addition-product in the case of diethylamine differs from the above, inasmuch as it is an oil which, on standing, gives benzamide.

Although in every case more or less hydrogen sulphide was evolved in the action of amines on the acylthioncarbamic esters, thus indicating the formation of acylpseudourea ethers, nevertheless these interesting compounds could not be isolated from the other by-products in these reactions (except in the case of ammonia). They form oils which cannot be distilled out of the mixture, without decomposition, even under reduced pressure. Their presence was established, however, not only by the fact that hydrogen sulphide was evolved, but also by the comparison of the properties of the reaction-products with those of the corresponding acylpseudourea ethers. We prepared the latter from the benzoylimidothiocarbonic esters, $C_6H_5CO—N=C\begin{matrix}SR\\OR\end{matrix}$, and it was found that the action of dilute hydrochloric acid affords a delicate test for their presence (see below).

The benzoylimidothiocarbonic esters are readily formed by the action of alkyl iodides on the sodium or potassium salts of the benzoylthioncarbamic esters,[1] in the same manner, as it has been found in general that the derivatives of the thioncarbamic esters react in the pseudoform, giving the substituted imidothiocarbonic esters:[2]

[1] Lössner: J. prakt. Chem., 1874 [2], **10**, 237; Dixon: J. Chem. Soc. (London), 1899, 380.

[2] Liebermann: Ann. Chem. (Liebig), **270**; Busch and Lingenbrink: Ber. d. chem. Ges., **32**, 2620; Fromm and Block: *Ibid.*, 2212; and Wheeler and Barnes: This JOURNAL, **24**, 60.

$$C_6H_5CONHCS.OC_2H_5 \rightarrow C_6H_5CO{-}N{=}C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix} \quad \text{(III)}.$$

Hitherto only one compound of this series has been isolated. Lössner obtained diethyl benzoylimidothiocarbonate (III) in the above manner. He states that it is an oil which decomposes at 44°, giving off mercaptan; while at higher temperatures benzonitrile and a syrupy residue are obtained. He assigned the incorrect formula, $C_6H_5CON(C_2H_5)CO.SC_2H_5$, to this substance, and the solid obtained by treating this with ammonia was regarded as benzoylethylurea. Dixon,[1] however, has shown that this is really a pseudourea.

The benzoylimidothiocarbonic esters, when prepared as described below, are oils without exception, which, as far as we have observed, distil unaltered under reduced pressure. For example, the oil of Lössner, when pure, has an odor like the xanthic esters, and it boils at about 210° at 19 mm. pressure, without the slightest sign of decomposition. The reaction which affords these oils is so smooth that for most purposes it is unnecessary to distil them. In some of our experiments the ether solutions of the crude products, after washing, were thoroughly dried over calcium chloride and then evaporated in a vacuum at 100°. Under these conditions the only impurity that appears to be present is benzamide, and then, if heating has been avoided before drying, only in very small quantities. When the oils are heated with water they give benzamide:[2]

$$\text{(IV)}\ C_6H_5CON{=}C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix} \rightarrow C_6H_5CONH_2 + CO_2 + C_2H_5OH + C_2H_5SH.$$

We find that with hydrogen sulphide at 100° the following takes place:

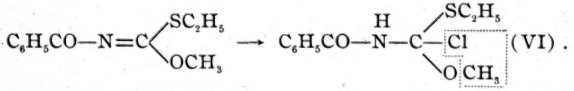
$$\text{(V)}\ C_6H_5CO{-}N{=}C\begin{matrix}SCH_3\\OCH_3\end{matrix} \rightarrow C_6H_5CON(H){-}C\begin{matrix}SCH_3\\SH\\OCH_3\end{matrix} \rightarrow C_6H_5CON(H){-}CS.OCH_3.$$

[1] *Loc. cit.*

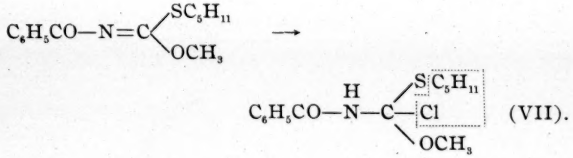
[2] Lössner: *Loc. cit.*

The ester is converted into benzoylthioncarbamic ester with loss of mercaptan.

That the oils obtained in the above manner are homogeneous is shown in each case by their smooth reactions with hydrogen chloride and with organic bases. We have obtained instances of the two following decompositions when the oils are dissolved in benzene and treated at ordinary temperatures with dry hydrogen chloride:



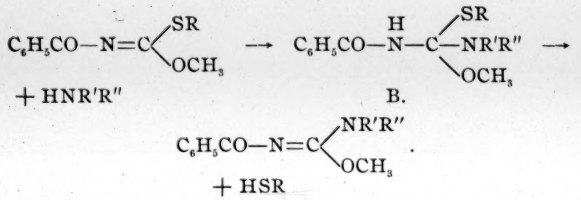
(VI).



(VII).

The decomposition with hydrogen chloride proceeds, with the series $C_6H_5CO-N=C(SAlk)(OCH_3)$ chiefly or entirely, according to reaction (VI), giving benzoylthiolcarbamic esters. When the alkyl group is amyl it separates according to reaction (VII).

When the benzoylimidothiocarbonic esters are treated with organic bases they readily react, giving off mercaptan and forming acylpseudourea ethers. The reaction is, in all probability, perfectly analogous to that of the above-mentioned benzoylthioncarbamic esters, except that the intermediate addition-product B (below) decomposes more smoothly and not in such a variety of ways as found in the case of the addition-product A. In most cases the reaction appears to take place quantitatively, as follows:



It appears that previously this action has only been investigated with ammonia, Dixon having shown that methyl- and ethyl-*ψ*-n-benzoylurea are formed in this way. He obtained these acylpseudourea ethers as crystalline compounds melting from 74°–75° and 77°–78°, respectively.

The compounds of this type which we have obtained with organic bases are oils. Those which we attempted to distil decomposed. They appear to be even more reactive than the interesting series of pseudourea ethers first obtained by Lengfeld and Stieglitz,[1] which have been so thoroughly studied by Stieglitz and Dains.[2] In properties they are closely similar to the acylimido esters[3] and acylamidines,[4] to both of which series the compounds belong, since they have the structure of both these classes combined. We find that the most striking reaction, at present, of this series of benzoylpseudourea ethers is the ease with which they act with hydrochloric acid. Most of the pseudourea ethers mentioned above, as well as those described by Stieglitz and McKee,[5] give salts with hydrochloric acid from which platinum double salts can be prepared. In stability, they approach the salts of the imido ethers prepared by Pinner and others. We observed similar properties among the benzoylpseudourea ethers in the case of those prepared with ammonia. For example, benzoylpseudoethylurea, $C_6H_5CO-N=C(NH)(OC_2H_5)$, dissolves in cold

[1] Ber. d. chem. Ges. (1894), **27**, 926.
[2] J. Am. Chem. Soc., **21**, 136.
[3] Wheeler and Walden: This JOURNAL, **19**, 129; Wheeler, Walden, and Metcalf: *Ibid.*, **20**, 64; and **19**, 217.
[4] Wheeler and Walden: *Ibid.*, **20**, 569.
[5] Ber. d. chem. Ges., **33**, 807.

hydrochloric acid, and gold chloride gives a bright-yellow precipitate of fine needles. A gold determination in this agreed with the formula, $C_6H_5CO-N=C\begin{matrix}NH_2\\OC_2H_5\end{matrix}.HCl.AuCl_3$. This salt is quite stable and it melts with decomposition at about 140°.

When, on the other hand, the more negative benzoylpseudourea ethers, especially those containing aryl groups, are treated with cold, aqueous hydrochloric acid, a reaction starts immediately. The solutions effervesce, alkyl chloride being driven off, whereupon, as a rule, the oils are quantitatively converted into beautifully crystallizable colorless acylureas. In the case of the aryl derivatives the oils crystallize immediately, while the alphyl compounds solidify more slowly.

This is in striking contrast to some of the pseudourea ethers of Stieglitz and Dains which are not completely decomposed by cold aqueous hydrochloric acid after a month's standing.

The following represents the course of the reaction with hydrochloric acid :

(IX.) $C_6H_5CO-N=C\begin{matrix}NRR'\\OCH_3\end{matrix} \longrightarrow C_6H_5CON(H)-C(NRR')(Cl)(OCH_3) \longrightarrow$

$$C_6H_5CONHCONRR' + CH_3Cl$$

This sensitiveness to hydrochloric acid finds a perfect parallel in the deportment of the acylimido esters, and it is shared also to a less extent by the acylamidines. The results show that the more negative the character of the radical in the imido ester grouping, $RN = CR'.OR''$, the more sensitive are the compounds in regard to decomposition by hydrogen chloride, a fact also noticed by Stieglitz and Dains in other cases.

In this connection it is interesting to note that pure water has little tendency to react with most of the benzoylpseudo-

urea ethers. This is well illustrated by the fact that Dixon, in showing the structure of the acylpseudourea ether,

$$C_6H_5CON{=}C\begin{matrix}NH_2\\OCH_3\end{matrix},$$

heated the compound in closed tubes with ten parts water from 105°–125° "without any sign of change. On raising the temperature to 150°–160° action occurred, carbonic anhydride escaped on opening the tube, the liquid contents of which smelt of ammonia and methyl benzoate." In other words, the material refused to react with water without total decomposition.

On the other hand, we find that if this compound which melts at 77° is gently warmed with water, in the presence of hydrochloric acid, it fuses, but in a few moments it solidifies, whereupon the material is quantitatively converted into benzoylurea, $C_6H_5CONHCONH_2$, melting at 214°. The above procedure affords a smooth method for the preparation of most of the α-β-benzoylureas since the different steps of the process give almost quantitative yields.

We hope later to describe other reactions of the acylpseudourea ethers.

The acylthioncarbamic esters react with phenylhydrazine, giving off hydrogen sulphide in the cold. The products, however, are not pseudourea or pseudosemicarbazidic esters, as might be expected, but the following ring-formed compounds:

$$\begin{matrix}CH_3.CO{-}NHCS.OCH_3\\+\\C_6H_5NH{-}NH_2\end{matrix}\longrightarrow\begin{matrix}CH_3.C{=}N{-}C{-}OCH_3\\|\qquad\quad||\\C_6H_5.N{-}\!-\!-{-}N\end{matrix}\qquad(X.)$$

That the products are alkyloxytriazoles is shown by the behavior of the compound from methyl benzoylthioncarbamate This, when boiled with hydrochloric acid, slowly gives up the methyl group and the so-called 1,5-diphenyl-3-oxytriazole (1,5-diphenyl-3-triazolone?) is obtained:

$$\begin{matrix}C_6H_5C{=}N{-}C.OCH_3\\|\qquad\quad||\\C_6H_5.N{-}\!-\!-{-}N\end{matrix}\longrightarrow\begin{matrix}C_6H_5C{=}N{-}CO\\|\qquad\quad|\\C_6H_5.N{-}\!-\!-{-}NH\end{matrix}.\qquad(XI.)$$

The product (XI.) is identical with that obtained by Young[1] from phenylsemicarbazide and benzaldehyde, and by Widman[2] from benzoylsemicarbazide by treating with alkali.

Phenylhydrazine, therefore, reacts with the thionacylurethanes in a different manner than with the ordinary acylurethanes, inasmuch as Andreocci[3] found that acetylurethane gives 1-phenyl-3-methyl-5-triazolone, while the above reactions lead to the formation of the isomeric compound, 1-phenyl-5-methyl-3-triazolone.

EXPERIMENTAL PART.

The Action of Acylthioncarbamic Esters with Organic Halides.

Preparation of Methyl Acetylthioncarbamate, $CH_3CO—NHCS.OCH_3$.—In our first experiments we boiled acetyl chloride in benzene solution with an excess of lead sulphocyanide for several hours; methyl alcohol was then added, in slight excess, and the mixture boiled for about thirty minutes. On evaporating, an oil was obtained, which, on cooling, solidified. It was crystallized from petroleum ether, when it separated in arborescent crystals melting at 79°–80°. It is readily soluble in water, alcohol, benzene, and chloroform, and when boiled with freshly precipitated mercuric oxide, it is desulphurized. A nitrogen determination gave :

	Calculated for $C_4H_7NO_2S$.	Found.
N	10.52	10.12

This compound is more easily obtained by warming methyl thioncarbamate with acetic anhydride on the water-bath. We found later that it is unnecessary to use lead sulphocyanide for the preparation of either acetyl or benzoyl rhodanide. In order to obtain a good yield of acetyl rhodanide, acetyl chloride is boiled with an excess of finely pulverized potassium sulphocyanide, in the presence of a little toluene, and under a pressure of about 900 mm. of mercury. In the case of benzoyl rhodanide, an increase in pressure is unnecessary, for example : 15 grams of benzoyl chloride were

[1] Ber. d. chem. Ges., **29**, 2311.
[2] *Ibid.*, **29**, 1951.
[3] *Ibid.*, **22**, R. 737.

boiled with 10.5 grams of potassium sulphocyanide in 10 cc. of toluene for fifteen minutes and then the material was distilled at 36–35 mm. pressure, when, below 90°, the toluene was collected; from 142°–151° only a few drops distilled over; and then from 151°–151°.5 the entire remainder was obtained except an insignificant colored residue. The last fraction consisted of practically pure rhodanide.

Methyl Acetylthiolcarbamate, $CH_3CO—NHCO.SCH_3$.—We observed the formation of this compound when 4 grams of methyl acetylthioncarbamate were allowed to stand with one molecular proportion of methyl iodide, in a sealed tube at 40°–45°, for three weeks. The material when crystallized from benzene, separated in the form of fine needles, melting from 145°.5–146°. It is insoluble in cold water, but readily soluble in hot water and in alcohol. It was not desulphurized when boiled with mercuric oxide, and a nitrogen determination gave:

	Calculated for $C_4H_7NO_2S$.	Found.
N	10.52	10.15

When methyl acetylthioncarbamate was heated with an excess of methyl iodide on the steam-bath for from six to seven hours no molecular rearrangement occurred, and no change was noticed when the mixture was allowed to stand at ordinary temperature for three weeks. That a rearrangement had taken place in the first experiment was shown by the fact that the compound melting at 145°.5–146° can also be prepared by warming methyl thiolcarbamate with acetic anhydride on the water-bath.

Ethyl Acetylthioncarbamate, $CH_3CO—NHCS.OC_2H_5$, was prepared like the methyl ester. Dixon[1] has shown that when pure acetyl rhodanide is mixed with alcohol a violent reaction takes place, fused sulphur and other products being obtained. However, this ester can be prepared from the rhodanide if the latter is mixed with benzene. It is difficultly soluble in water, but readily soluble in alcohol and benzene. From water it crystalliizes in prisms and melts from 100°–101°. A nitrogen determination gave:

[1] J. Chem. Soc. (London), **61**, 529.

	Calculated for $C_5H_9NO_2S$.	Found.
N	9.5	9.9

Attempts to arrange this thion ester into the isomeric thiol compound were without success. When heated with ethyl iodide in a closed tube to 100°, ammonium iodide was obtained as the only solid product. When heated from 80°–90° a product was obtained crystallizing in plates and melting at 105°–106°, and otherwise having all the properties of ethyl thiolcarbamate, $H_2NCO.SC_2H_5$. When allowed to stand dissolved in ethyl iodide for four months, no action was observed. This is in marked contrast with the ease with which xanthogenamide and ethyl thionphenylcarbazinate undergo a molecular rearrangement.

Methyl Benzoylthioncarbamate, $C_6H_5CO—NHCS.OCH_3$.—This and the following ethyl ester were prepared by boiling benzoyl chloride, diluted with a little toluene, with an excess of potassium sulphocyanide. For 100 grams of benzoyl chloride the reaction was practically complete in a few hours; then, on cooling, alcohol was added and warmed for a short time. The toluene was then removed in a current of steam and the residue crystallized from dilute alcohol, when the ester separated in needles melting at 97°, as stated by Miquel.[1]

Methyl Benzoylthiolcarbamate, $C_6H_5CO—NHCO.SCH_3$.—This compound was obtained when 8 grams of the above ester were heated with methyl iodide in a closed tube from 80°–90° for six hours. On opening the tube it was found to be filled with a mass of beautiful, long prisms, some of them from 1–2 inches in length. On crystallizing these from alcohol they melted from 152°–153°, and a nitrogen determination gave :

	Calculated for $C_9H_9NO_2S$.	Found.
N	7.1	6.9

This thiol ester is soluble in alkali and is precipitated unaltered by acids. When boiled with mercuric oxide it gave no precipitate of mercuric sulphide, thus differing from the thion ester.

[1] *Loc. cit.*

When the thion ester was heated with methyl iodide to 100°–110° decomposition took place, and a compound free from sulphur and difficultly soluble in alcohol was obtained. It was insoluble in hot water and sodium hydroxide, and it separated from alcohol in small needles, melting at about 215° with effervescence. It crystallizes unaltered from nitric acid, and a nitrogen determination gave 11.1 per cent. It was not identified.

Ethyl Benzoylthioncarbamate, $C_6H_5CO—NHCS.OC_2H_5$.—This compound was first obtained by Lössner,[1] the structure $\begin{matrix} C_6H_5CO \\ C_2H_5 \end{matrix}\!\!>\!NCO.SH$ being assigned to it, while in Beilstein's "Handbuch" it is represented by the formula

$$C_6H_5CONHCO.SC_2H_5\,(?).$$

Its correct formula, the thion structure, was given to it by Miquel[1] and further confirmed by Dixon.[1] For our use we prepared it from the rhodanide as above stated. It forms colorless needles from dilute alcohol and it melts from 73°–74°. It is desulphurized by boiling with mercuric oxide, and it has little if any tendency to undergo a molecular rearrangement with ethyl iodide. It was not changed by standing for two weeks with ethyl iodide or by heating it from 95°–100° or from 100°–110°. When heated with the iodide from 125°–130° for four hours benzamide was obtained.

Benzoylcarbaminthioglycollic Acid, $C_6H_5CONHCO.SCH_2COOH$.—When molecular quantities of methyl benzoylthioncarbamate and chloracetic acid were heated for eight hours on the steam-bath, a slow effervescence took place. The product then crystallized from dilute alcohol gave colorless needles melting from 169°–170°. This material was not desulphurized by boiling with mercuric oxide. It is soluble with difficulty in benzene, and a nitrogen determination gave:

	Calculated for $C_{10}H_9NO_4S$.	Found.
N	5.8	6.1

[1] *Loc. cit.*

Benzoylurea, $C_6H_5CO-NHCONH_2$.—On treating the above compound, dissolved in alcohol, with ammonia, a mass of small lozenge-shaped plates separated. This material was free from sulphur and melted from 214°–215° with slight effervescence. It was soluble in hot water and in sodium hydrate and was precipitated from the latter solution unaltered by hydrochloric acid. A nitrogen determination gave:

	Calculated for $C_8H_8N_2O_2$.	Found.
N	17.0	16.7

It was stated by Zinin,[1] who first obtained benzoylurea, that this compound melts "gegen 200°". Geuther, Scheitz, and Marsh[2] give 208°. That these melting-points are too low is shown by the above; moreover, we have obtained benzoylurea by other methods and in each case it was found to melt at 214°–215°.

Methyl Dibenzoylthioncarbamate, $(C_6H_5CO)_2NCS.OCH_3$.—The sodium salt of methyl benzoylthioncarbamate was prepared by dissolving the ester in methyl alcohol, adding a strong solution of sodium methylate, and then precipitating with ether. Thus prepared it forms a sandy powder which was dried over sulphuric acid in a vacuum. On treating this, suspended in benzene, with the calculated quantity of benzoic anhydride, and boiling for six hours, an oil was obtained which solidified on cooling. On crystallizing this from petroleum ether, colorless plates separated which melted, when pure, from 81°–82°, and a nitrogen determination gave the following result:

	Calculated for $C_{16}H_{13}NO_3S$.	Found.
N	4.6	4.7

When this diacylthiourethane was treated with a molecular proportion of phenylhydrazine in the cold, hydrogen sulphide was evolved and, on crystallizing the product from benzene, needles or prisms were obtained melting from 166°–167°, which proved to be benzoylphenylhydrazine.

When the sodium salt of methyl benzoylthioncarbamate

[1] Ann. Chem. (Liebig), **92**, 404.
[2] Ztschr. Chem., 1868, 305.

was treated in dry benzene with acetic anhydride, and the product crystallized from dilute alcohol, nothing but unaltered ester was obtained.

Methylene Thiolcarbamate, $H_2NCO.SCH_2S.CONH_2$.–Gabriel and Heyman[1] found that ethylene bromide and thioamides give thiazoline derivatives, while Pinkus[2] obtained from trimethylene chlorobromide and thioamides the so-called penthiazolines. In the case of xanthogenamide, he found that the reaction gave a compound or mixture agreeing with the formula, $C_4H_8NOS\frac{Br+Cl}{2}$. Recently Busch[3] has found that the potassium salts of the dithiocarbazinic esters give ring-formed compounds with ethylene bromide, diazthins, and not the ethylene esters. In a recent paper Wheeler and Barnes[4] have described the action of ethylene bromide on xanthogenamide. They obtained a product which appeared to be the ethylene ester of thiolcarbamic acid. It therefore seemed of interest to determine whether other alkyl dihalides also act abnormally with xanthogenamide. For this purpose we warmed methylene iodide with xanthogenamide in molecular proportions for five hours on the steam-bath, when the odor of the iodide disappeared. On cooling and crystallizing from water, small compact crystals were obtained, melting from 168°–170°, which, on analysis, gave the following result:

	Calculated for $C_3H_6O_2N_2S_2$.	Found.
N	16.8	16.3

Ethylene Thiolcarbamate, $H_2NCO_2SCH_2—CH_2S.CONH_2$, from ethylene bromide and xanthogenamide, has already been described,[5] but the melting-point was omitted; it melts from 231°–232°.

Trimethylene Thiolcarbamate, $H_2NCO.SCH_2CH_2CH_2S.CONH_2$, from trimethylene bromide and xanthogenamide, after two hours' heating on the water-bath, crystallizes from hot water in plates, and melts from 177°–179°. It is extremely soluble

[1] Ber. d. chem. Ges., **23**, 157; **24**, 783.
[2] *Ibid.*, **26**, 1083.
[3] J. prakt. Chem., **60**, 26.
[4] This JOURNAL, **22**, 151.
[5] Wheeler and Barnes: *Loc. cit.*

in alcohol and difficultly soluble in benzene. A nitrogen determination gave:

	Calculated for $C_5H_{10}O_2N_2S_2$.	Found.
N	14.4	14.1

When *isobutylene bromide* and xanthogenamide were heated on the water-bath for five hours cyanuric acid, ethyl thiolcarbamate, and unaltered material were obtained.

The Behavior of Acylthioncarbamic Esters with Ammonia and Amines.

Ethyl Benzoylthioncarbamate and Ammonia.—Five grams of the ester were dissolved in an excess of alcoholic ammonia and the solution allowed to stand at rest for three days. The action began immediately, and hydrogen sulphide was slowly evolved at ordinary temperatures. After the action was complète the alcohol was distilled off, and the first portions were tested for mercaptan, but with a negative result. When most of the alcohol had evaporated, the remaining solution was poured into dilute potassium hydrate, when an oil separated which soon solidified. On crystallizing this from petroleum ether, beautiful, long, needle-like prisms separated, which melted sharply from 74°–75°. This compound has practically the same melting-point as ethyl benzoylthioncarbamate; that it was not this substance was shown by mixing the two, when the mixture melted at 45°. The properties of the substance show that it is identical with the compound first obtained by Lössner, which Dixon has shown has the formula,

$$C_6H_5CO-N=C\begin{matrix}NH_2\\OC_2H_5\end{matrix}.$$ [1]

In other words, it is *benzoylpseudoethylurea*. The reaction appears to be practically quantitative. When this substance is treated with dilute hydrochloric acid it dissolves, and on gently warming the solution and again cooling *benzoylurea*, melting from 214°–215°, separates.

Benzoylpseudoethylurea Chloraurate, $C_6H_5CO-N=C(NH_2).OC_2H_5.HCl.AuCl_3$, is precipitated from the above hydrochloric

[1] *Loc. cit.*

acid solution on the addition of gold chloride. It forms fine, bright-yellow needles, which are difficultly soluble in water and melt at about 140°. A gold determination gave:

	Calculated for $C_{10}H_{13}N_2O_2Cl_4Au$.	Found.
Au	37.0	37.1

Methyl Benzoylthioncarbamate and Diethylamine unite at ordinary temperature, without evolution of gas, to form a varnish which refused to solidify on cooling or on keeping in a vacuum desiccator over sulphuric acid for two to three days. At the end of this time free amine appeared to be absent and a nitrogen determination gave 9.89 per cent nitrogen instead of 10.49, which is required for

$$C_6H_5CONHCS.OCH_3.HN(C_2H_5)_2.$$

The result is, perhaps, as close as could be expected, considering the fact that the material does not permit of a better method of purification. The material, on standing for three weeks in a desiccator, deposited benzamide. On heating, the result was the same; hydrogen sulphide and other products were given off, and only a small amount of oil besides benzamide was obtained. It dissolves very readily in alcohol and benzene, and is precipitated as an oil by petroleum ether.

Ethyl Benzoylthioncarbamate and Diisobutylamine combine to form a varnish as in the previous case. When 16 grams of the ether were heated with 10 grams of the amine, reaction began at about 80° and 600 cc. of hydrogen sulphide were collected over water, and the presence of alcohol and mercaptan was also identified in the volatile products. On cooling, a thick oil was obtained which, when treated with hydrochloric acid, gave off ethyl chloride and solidified completely. On crystallizing then from strong alcohol, colorless prisms separated which occurred in twins, in the form of beautiful crosses, and melted at 130°–132°. This material was found to contain sulphur, and a nitrogen determination agreed with the calculated for *benzoyldiisobutylthiourea*, $C_6H_5CONHCSN(C_4H_9)_2$.

	Calculated for $C_{16}H_{26}N_2OS$.	Found.
N	9.59	9.95

A portion of the above product, which had not been treated with hydrochloric acid, was distilled at 25 mm. pressure, when, after decomposition of some constituent (the pseudourea ether (?)), a considerable portion of oil distilled over between 182°–190°. This was redistilled at ordinary pressure when it boiled mostly from 288°–311°; it was then treated with alkali and the insoluble part was extracted with ether, whereupon, on evaporating, a brilliant mass of stout prisms separated. This compound was purified by crystallizing from petroleum ether. It melted at 65°, and a nitrogen determination agreed with the calculated for *diisobutylbenzamide:*

$$C_6H_5CO—N(C_4H_9)_2.$$

	Calculated for $C_{15}H_{23}NO$.	Found.
N	6.0	6.4

The alkaline solution on acidifying gave benzoyldiisobutylthiourea. Diisobutylbenzamide, like its homologues, is very soluble in most organic solvents, from which solutions it is obtained as an oil which solidifies to form beautiful crystals.

Methyl Benzoylthioncarbamate and Diisoamylamine combine with a decided evolution of heat, to form an oil which quickly solidifies. No trace of mercaptan or hydrogen sulphide is given off at ordinary temperatures and, when this addition-product is prepared by mixing molecular quantities, it melts at 55°–60°. It is extremely soluble in benzene and alcohol, and apparently undergoes dissociation, since petroleum ether precipitates unaltered methyl benzoylthioncarbamate. On standing in a desiccator over sulphuric acid, it slowly decomposed, becoming oily (separation of free amine), when after a week unaltered ester was obtained. As it could not be purified by crystallization, a portion was prepared by mixing 5 grams of the ester with about 4 grams of diamylamine and grinding the material together in a mortar, after which it was thoroughly pressed on paper and allowed to stand exposed to the air for a short time. A nitrogen determination then gave 8.6 per cent of nitrogen while the calculated for

$$C_6H_5CONHCSOCH_3.HN(C_5H_{11})_2$$

is 7.9 per cent; the calculated for unaltered ester being 7.1 per cent.

When the addition-product was heated, evolution of hydrogen sulphide and mercaptan were noticed at its melting-point, and, on maintaining the temperature at about 80°, an oil was obtained which, when treated with benzene, deposited plates. These were crystallized from water, whereupon they melted from 126°–127°; they were free from sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzamide*.

	Calculated for C_7H_7NO.	Found.
N	11.5	11.2

An attempt was made to isolate the pseudourea ether that is formed here, which constitutes the oil removed by benzene in the above experiment. With this object we tried distilling the addition-product at 15 mm. pressure; on heating, the pressure rose to 40 mm., and up to 200° an oil and a solid distilled over. The oil consisted mostly of benzonitrile and the solid was benzamide. When this pseudourea ether is treated with cold hydrochloric acid, methyl chloride is evolved and benzamide and diamylamine hydrochloride are obtained. The formation of benzoyldiisoamylurea was not observed.

Ethyl Benzoylthioncarbamate and Benzylamine energetically react with evolution of heat, hydrogen sulphide and mercaptan are apparently evolved, and the mixture readily solidifies. On crystallizing then from 95 per cent alcohol, flattened prisms separate which melt sharply at 89°. The material does not contain sulphur, and a nitrogen determination agrees with the calculated for *benzoylbenzylurea*,

$$C_6H_5CONHCONHCH_2C_6H_5.$$

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.0	10.7

Ethyl Benzoylthioncarbamate and Aniline.—Ten grams of the former were mixed with one molecular proportion of the latter and the mixture was warmed for from eight to nine hours on the steam-bath, when hydrogen sulphide ceased being

evolved and an oil was obtained. On standing, crystals separated which formed an arborescent mass from dilute alcohol, and melted from 202°–203°. This material was free from sulphur, and a nitrogen determination gave the following result:

	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
N	11.66	11.68

This material agrees in properties with *benzoylphenylurea*, $C_6H_5CONHCONHC_6H_5$, which Blacher[1] has prepared by another method. He gives its melting-point as 204°–205°. This compound has also been obtained by Kuhn,[2] who states that it melts at 199°, and also by Beckmann and Köster, who give 204° as its melting-point.

Ethyl Benzoylthioncarbamate and Paratoluidine.—A mixture of these substances in molecular proportions were heated for from seven to eight hours on the steam-bath. Hydrogen sulphide was given off during the reaction; the product thus contained consisted chiefly of pseudoethylparatolylbenzoylurea, $C_6H_5CON = C(OC_2H_5)—NHC_6H_4CH_3$, and was an oil which on exposure to the laboratory atmosphere deposited crystals after two days. On pressing these on a plate and crystallizing from dilute alcohol, small narrow prisms were obtained which melted from 80°–81°. These were free from sulphur, and a nitrogen determination showed that this material was *benzoylparatolylurea*, $C_6H_5CO—NHCONHC_6H_4CH_3$.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.0	10.7

In order to show the presence of pseudoethylparatolylurea, 3 grams of methyl benzoylcarbamate and 1.6 grams of toluidine were heated together; a lively effervescence of hydrogen sulphide took place at 90°, and in about one hour, with these quantities, it practically ceased. The oil thus obtained was treated with 10 cc. of about 20 per cent hydrochloric acid, and the gas which was evolved was collected over water, in which it was partly soluble. In one hour over 80 cc. of methyl chlo-

[1] Ber. d. chem. Ges., **28**, 435.
[2] *Ibid.*, **17**, 2881.
[3] Ann. Chem. (Liebig), **274**, 28.

ride were obtained. When methyl benzoylthioncarbamate was treated with hydrochloric acid under the same conditions, no gas was evolved. On warming, however, methyl chloride is evolved.

With the object of isolating the pseudourea ether that is formed in this reaction, we subjected the reaction-product to distillation, starting at 13 mm. pressure. At 165° the pressure rose, and up to 200°, at 20 mm. pressure, a portion had distilled over; in this we identified benzamide and benzonitrile, which showed that the material had decomposed.

When ethyl acetylthioncarbamate was warmed with *p*-toluidine, hydrogen sulphide was evolved, and an oil and a solid were obtained; on crystallizing the solid from alcohol, it melted at 147° and had all the properties of paracettoluide. The oil was not examined.

Ethyl Benzoylthioncarbamate and 2,4-Dimethylaniline were heated together in molecular proportions on the water-bath, and an attempt was made to collect the mercaptan given off, but it was carried off in the stream of hydrogen sulphide which escaped. On cooling, an oil was obtained together with some solid. The solid was filtered off and, on crystallizing from alcohol, it melted from 215°–217°. On treating the oil with hydrochloric acid, ethyl chloride was evolved and the material solidified when, on crystallizing from alcohol, it likewise melted from 215°–217°. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O_2$.	Found.
N	10.4	10.5

This compound is therefore *α,β-benzoylmetaxylylurea*,

$$C_6H_5CONHCONHC_6H_3(CH_3)_2.$$

Ethyl Benzoylthioncarbamate and p-Anisidine reacted at once with a rapid evolution of hydrogen sulphide. When warmed on the water-bath until this ceased, and then cooled, very little oil was obtained. The chief quantity of the reaction-product was solid. From this, two compounds were separated by means of alcohol and benzene. The more soluble one, the chief product, proved to be benzoylparaanisidine. Boiling the product with alcohol gave a mass of colorless prisms

which melted from 216°–218°, and a nitrogen determination of this substance, which burns slowly, gave the following result:

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	10.3	9.8

This material is therefore *benzoylparamethoxyphenylurea*,

$$C_6H_5CONHCONHC_6H_4OCH_3.$$

When the above oil was treated with hydrochloric acid, it gave off ethyl chloride, showing the presence of benzoyl-pseudoethylparamethoxyphenylurea.

Methyl Benzoylthioncarbamate and α-Naphthylamine.—On warming molecular quantities of these substances until hydrogen sulphide ceased coming off, an oil was obtained which, treated with benzene and petroleum ether, gave a precipitate. When this was boiled with alcohol a residue of cyanphenine, melting at 230°, remained. On adding water to the alcoholic solution, and then crystallizing from dilute alcohol, we obtained colorless prisms melting from 165°–166°. This material contained no sulphur. That it was not benzoyl-α-naphthalide, which melts at 160°–162°, was shown on mixing these substances, when the mixture melted at 140°. A nitrogen determination agreed with the calculated for *benzoyl-α-naphthylurea*, $C_6H_5CONHCONHC_{10}H_7$.

	Calculated for $C_{18}H_{14}N_2O_2$.	Found.
N	9.6	9.8

Methyl Benzoylthioncarbamate and β-Naphthylamine gave off hydrogen sulphide on warming, thus showing the formation of a pseudourea ether. The product was obtained as an oil that deposited nothing solid on standing a week. On adding petroleum ether and crystallizing from dilute alcohol, small needles separated which melted at 156°. The material contained no sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzoyl-β-naphthalide*.

	Calculated for $C_6H_5CONHCONHC_{10}H_7$.	Calculated for $C_6H_5CONHC_{10}H_7$.	Found.
N	9.65	5.46	5.26

Ethyl Benzoylthioncarbamate and Diphenylamine react with

difficulty and hydrogen sulphide is given off. After heating for three days on the steam-bath an oil was obtained which, when treated with hydrochloric acid, decomposed with the separation of diphenylamine.

Ethyl Benzoylthioncarbamate and Orthophenylenediamine were mixed in the proportion of 2 molecules of the former to 1 of the latter in ether solution, when, on evaporating, hydrogen sulphide was given off and a solid was directly obtained. There appeared to be little or no oil in this case. The material, when crystallized from alcohol, separated in lozenge-shaped crystals, which were free from sulphur; they melted at 235°, and a nitrogen determination agreed with the calculated for *dibenzoylphenylen diurea*,

$$C_6H_5CONHCONHC_6H_4NHCONHCOC_6H_5.$$

	Calculated for $C_{28}H_{18}N_4O_4$.	Found.
N	13.9	14.2

Methyl Benzoylthioncarbamate and Phenylhydrazine.—When phenylhydrazine is added to the ester, the mixture becomes warm and hydrogen sulphide is given off. On heating, to complete the action, and then cooling, an oil is obtained which readily solidifies. On crystallizing this from dilute alcohol, colorless needles are obtained melting from 85°–86°. A nitrogen determination agreed with the calculated for *1,5-diphenyl-3-ethoxytriazole*. This material was free from sulphur.

	Calculated for $C_{15}H_{13}N_3O$.	Found.
N	16.7	16.9

1,5-Diphenyl-3-triazolone was obtained when the above was boiled with concentrated hydrochloric acid in alcoholic solution for from eight to nine hours.

Ethyl Acetylthioncarbamate and Phenylhydrazine reacted in the cold, giving off hydrogen sulphide, but on standing two weeks nothing solid separated. The material was then distilled at 17–18 mm. pressure, whereupon it practically all boiled from 190°–193°. This readily solidified and, on crystallizing from petroleum ether, it formed long, stout prisms,

melting at 49°–50°. It is extremely soluble in alcohol and benzene, and a nitrogen determination gave results agreeing with the calculated for *1-phenyl-5-methyl-3-ethoxytriazole.*

	Calculated for $C_{11}H_{13}N_3O$.	Found.
N	20.7	20.9

On the Benzoylimidothiocarbonic Esters and Their Behavior with Hydrogen Chloride.

Diethyl Benzoylimidothiocarbonate, $C_6H_5CON = C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}$.

We have prepared a series of these esters by treating the potassium salts of the benzoylthioncarbamic esters, in alcoholic solution, with alkyl iodides. Warming, during this process, must be avoided, since, otherwise, as found by Lössner in the case of the preparation of the diethyl ester,[1] mercaptan is evolved, and the oils suffer more or less decomposition with the formation of benzamide. The potassium salts of the benzoylthioncarbamic esters crystallize more readily than the sodium salts. In order to prepare them, alcoholic potash is added to a strong solution of the ester in alcohol when a crystalline mass separates at once. On treating the potassium salt of ethyl benzoylthioncarbamate suspended in alcohol with ethyl iodide, the mixture, after standing twelve hours, no longer had an alkaline reaction. Water was then added, and the precipitated oil was extracted with ether, washed, and then thoroughly dried over calcium chloride. On evaporating and distilling the oil at 19 mm. pressure, the material all boiled from 209°–212°, almost from the first to the last drop. There was no sign of decomposition and the yield is almost quantitative, a portion being lost in treating the alcohol solution with water. Thus obtained, ethyl benzoylimidothiocarbonate is a colorless oil of a faint odor, resembling the xanthic esters. Without further purification of the oil a nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2S$.	Found.
N	5.9	6.2

[1] *Loc. cit.*

Dimethyl Benzoylimidothiocarbonate, $C_6H_5CON=C\begin{matrix}SCH_3\\OCH_3\end{matrix}$, was obtained when 46 grams of methyl benzoylthioncarbamate, 9.5 grams of potassium hydrate, and 33.5 grams of methyl iodide were mixed in methyl alcohol. The mixture became warm, and the odor of mercaptan was noticed; this greatly increased on attempting to distil off the methyl alcohol after the action was complete. The heating was then stopped and cold water was added, and the oil was extracted with ether, whereupon, on evaporating, 22 grams of this ester were obtained, which, on standing, deposited plates of benzamide. These were filtered and the oil, without further purification, was used for the following experiments:

About 1 gram of the oil was dissolved in benzene and hydrogen chloride was passed in; warming and effervescence took place, and a mass of colorless needles separated, which melted from 152°–153° and were identical in every respect with *methyl benzoylthiolcarbamate*, $C_6H_5CO—NHCO.SCH_3$, described above.

Three grams of the oil were heated on the water-bath for about an hour and a half in a stream of hydrogen sulphide, mercaptan (?) and some methyl alcohol condensed in the delivery tube and, on cooling, dissolving in potassium hydrate and precipitating with hydrochloric acid, needles were obtained. When these were crystallized from dilute alcohol they were found to be *methyl benzoylthioncarbamate*,

$$C_6H_5CONHCS.OCH_3,$$

described above. When this oil is allowed to stand in water it remains liquid for weeks. On exposure, the crude oil evaporated, leaving benzamide.

Benzoylimidomethylthiolethylcarbonate, $C_6H_5CON=C\begin{matrix}SC_2H_5\\OCH_3\end{matrix}$, was prepared like the above diethyl ester. It was distilled at 20 mm. pressure when it boiled for the most part at about 210°. It then did not solidify in a freezing-mixture and in properties it resembled the diethyl compound. When this oil

was treated in dry benzene with hydrogen chloride it evolved methyl chloride and gave *ethyl benzoylthiolcarbamate*,

$$C_6H_5CONHCO.SC_2H_5,$$

which, on evaporating the benzene and crystallizing from dilute alcohol, separated in long, slender prisms melting from 105°–107°. It is soluble in sodium hydrate, and a nitrogen determination gave :

	Calculated for $C_{10}H_{11}NO_2S$.	Found.
N	7.0	6.7

An attempt to prepare this ester by warming ethyl thiolcarbamate, $H_2NCO.SC_2H_5$, with benzoic anhydride under conditions that were found to be favorable in the case of the corresponding acetyl compound, resulted in the formation of *cyanphenine* and a body which crystallized from alcohol in needles and melted finally from 167°–168°. This material contained sulphur, and a nitrogen determination gave results agreeing with the calculated for benzoyl rhodanide, the compound probably being the polymeric modification described by Miquel,[1] who states that it melts at 160°.

	Calculated for $(C_6H_5CO—NCS)_3$.	Found.
N	9.1	9.6

Benzoylimidomethylthiolisopropylcarbonate, $C_6H_5CON=C\begin{matrix}SC_3H_7\\OCH_3\end{matrix}$.—Isopropyl iodide reacts more slowly on the potassium salt of methyl benzoylthioncarbamate than the lower alkyl iodides. When 10 grams of the ester are used it is necessary to let the mixture stand for about three or four days. When the product was treated with hydrogen chloride it gave

Isopropyl Benzoylthiolcarbamate, $C_6H_5CONHCO.SC_3H_7$.—This crystallizes from alcohol in colorless prisms, which melt from 136°–137°. It is soluble in alkali, and a nitrogen determination gave :

	Calculated for $C_{11}H_{13}NO_2S$.	Found.
N	6.2	6.2

[1] Ann. chim. phys. [5], 11, 269.

Benzoylimidomethylthiolisobutylcarbonate,

$C_6H_5CON = C\begin{matrix}SC_4H_9\\OCH_3\end{matrix}$, is an oil like the preceding. It required from two to three days for its preparation. When dry hydrogen chloride is led into its solution in benzene, it evolves methyl chloride and gives

Isobutyl Benzoylthiolcarbamate, $C_6H_5CONHCO.SC_4H_9$, which crystallizes from dilute alcohol in thin plates or scales and melts at 115°–117°. It is insoluble in water but readily soluble in benzene and sodium hydrate, and a nitrogen determination gave :

	Calculated for $C_{12}H_{15}NO_2S$.	Found.
N	5.9	6.0

Benzoylimidomethylthiolisoamylcarbonate,

$C_6H_5CON = C\begin{matrix}SC_5H_{11}\\OCH_3\end{matrix}$.—In this case the action was complete in two days, it being hastened finally by warming. The oil, without distilling, was dried in a vacuum at 100°, when a nitrogen determination indicated the presence of benzamide.

	Calculated for $C_{14}H_{19}NO_2S$.	Found.
N	5.28	6.0

On standing, some benzamide separated. When this oil was treated with dry hydrogen chloride and the material purified by means of alkali and dilute alcohol, a compound crystallizing in needles was obtained, which melted at 96°. A nitrogen determination gave results which agreed with the calculated for *methyl benzoylthioncarbamate*, the calculated being 7.1 per cent, while 6.9 per cent was found. The calculated for the expected isoamyl benzoylthiolcarbamate is 5.5 per cent. The compound obtained had all the properties of the benzoylthionmethyl ester described above. This is the first exception to the rule that thiolcarbamic esters are formed by the action of hydrogen chloride on the imidothiolcarbonates.

On the Behavior of Benzoylimidothiocarbonic Esters with Amines and on the Behavior of Benzoylpseudoureas with Hydrochloric Acid.

As stated in the introduction, the behavior of the benzoyl-

imidothiocarbonic esters with bases has been investigated only in the case of ammonia.[1] We show below that the benzoylimidothiocarbonic esters readily react also with alkyl and aryl amines giving benzoylpseudourea ethers. Attempts to purify these compounds by distillation, in certain cases, were not crowned with success. Their behavior, however, with hydrochloric acid is described as the most characteristic reaction or simple test for their presence that we have observed, since by this treatment they evolve alkyl chloride and are, in most cases, quantitatively converted into the corresponding, easily crystallizable, benzoylureas.

Benzoylpseudomethylurea, $C_6H_5CO—N=C\begin{matrix}NH_2\\OCH_3\end{matrix}$. — This compound was prepared from benzoylimidomethylthiolisopropyl carbonate and alcoholic ammonia by allowing the mixture of these substances to stand for twelve hours, whereupon isopropyl mercaptan separated and the compound obtained by Dixon, in a similar manner, was obtained. It melted at 77° and agreed with his description. On treating this with 20 per cent hydrochloric acid, a reaction did not start immediately but, on gently warming, the material melted, then solidified, and, on crystallizing from alcohol, small lozenge-shaped plates separated, melting at 214° with effervescence. This material had all the properties of *benzoylurea*,

$$C_6H_5CONHCONH_2,$$

described above.

Benzoylpseudomethylethylurea, $C_6H_5CO—N=C\begin{matrix}NHC_2H_5\\OCH_3\end{matrix}$. —This was prepared from benzoylimidomethylthiolisopropylcarbonate by allowing a little less than 1 gram of the ester to stand for several days with a 33 per cent aqueous solution of ethylamine mixed with enough alcohol to form a solution. On then evaporating, an oil was obtained which was treated, without further handling, with 20 per cent hydrochloric acid, whereupon it was converted into

[1] Dixon : *Loc. cit.*

α,β-Benzoylethylurea, $C_6H_5CONHCONHC_2H_5$.—On standing, this separated from the hydrochloric acid solution in long needle-like prisms, some over 2 cm. in length. The preparation of this compound by a new method is of interest, because of the discrepancy between the melting-points recorded for this compound by Miquel,[1] Leuckart,[2] and Dixon.[3] These authors give 192°, 168°, and 114°–114°.5. On crystallizing our material from petroleum ether it melted sharply at 114° and agreed in all respects with the compound prepared by Dixon from *α,β*-benzoylethylthiocarbamide by desulphurization, so that evidently this is the correct melting-point for the substance.

Benzoylpseudomethylisobutylurea, $C_6H_5CO—N=C\begin{matrix}NH.C_4H_9\\OCH_3\end{matrix}$.

—When isobutylamine is mixed with benzoylimidomethyl thiolethylcarbonate the mixture starts to boil immediately, giving off ethyl mercaptan, and cooling is necessary. The product is an oil which, when treated with hydrochloric acid, slowly gives off methyl chloride and solidifies, forming

Benzoylisobutylurea, $C_6H_5.CONHCONHC_4H_9$.—This was crystallized from alcohol when long, slender prisms were obtained, melting sharply at 115°. A nitrogen determination gave:

	Calculated for $C_{12}H_{16}N_2O_2$.	Found.
N	12.7	12.9

Benzoylpseudomethyldiisoamylurea,

$C_6H_5CO—N=C\begin{matrix}N(C_5H_{11})_2\\OCH_3\end{matrix}$. —When benzoylimidothiolmethyl carbonate and diamylamine are mixed, reaction starts in the cold. The material was warmed to 60° until methyl mercaptan ceased being evolved, when hydrogen sulphide was passed in for several hours. On cooling, a mass of plates separated; these proved to be benzamide. On filtering and distilling at 13 mm. pressure, diisoamylamine, boiling at 72°, benzonitrile, and benzamide formed the chief products. An

[1] Ann. chim. phys. [5], **11**, 318.
[2] J. prakt. Chem. [2], **21**, 33.
[3] J. Chem. Soc. (London), 1899, 383.

appreciable amount of diamylthionmethylcarbamate was not obtained.

This and the corresponding ethylbenzoylpseudourea ether differ from most of the other urea ethers that we have examined by the fact that, although they give off alkyl chloride with hydrochloric acid, nevertheless, a body corresponding to benzoyldiisoamylurea was not obtained. A number of experiments were tried with hydrochloric acid under different conditions, but in every case nothing but benzamide and diisoamyl hydrochloride could be isolated. This behavior is in accordance with the ease with which the addition-product in the case of ethyl benzoylthioncarbamate and diisoamylamine gives benzamide and free amine. When *pseudoethylbenzoyldiisoamylurea* was prepared from benzoylimidothioethylcarbonate and diamylamine, and the product treated with hydrochloric acid, ethyl chloride was evolved, and again nothing but benzamide and amine hydrochloride was found.

Benzoylpseudomethylphenylurea, $C_6H_5CON{=}C\begin{matrix}NHC_6H_5\\OCH_3\end{matrix}$.—Benzoylimidomethylthiolethyl carbonate and aniline readily react when mixed, and the action may be hastened by warming on the water-bath. After the evolution of ethyl mercaptan had ceased, in one experiment, we attempted to purify the product by distilling at 16 mm. pressure. Both the temperature and pressure rose steadily, the material beginning to boil at 70°. At this pressure, when the temperature rose to 200°, benzonitrile and other products distilled over, leaving a mass of tar in the distilling bulb.

When this crude pseudourea ether is treated with hydrochloric acid, it reacts at once, solidifying and giving off methyl chloride, and, on crystallizing the product from alcohol, benzoylphenylurea, melting at 202°–203°, is obtained. It is identical with the product obtained from ethylbenzoylthioncarbamate and aniline described above.

Benzoylpseudoethylphenylurea, $C_6H_5CO{-}N{=}C\begin{matrix}NHC_6H_5\\OC_2H_5\end{matrix}$, from 2 grams of aniline and 4.8 grams of benzoylimidothiol-

diethylcarbonate, formed a clear light-yellow oil, after heating for some time in a vacuum on the steam-bath. A preparation made in this manner was analyzed with the following result:

	Calculated for $C_{16}H_{16}N_2O_2$.	Found.
N	10.4	10.8

Benzoylpseudomethyl-m-chlorphenylurea, $C_6H_5CON=C\begin{matrix}NHC_6H_4Cl\\OCH_3\end{matrix}$, was obtained from metachloraniline and benzoylimidomethylthiolethyl carbonate after eight hours' heating on the water-bath. It was converted directly by hydrochloric acid into *benzoylmetachlorphenylurea*,

$$C_6H_5CONHCONHC_6H_4Cl,$$

which crystallizes in needles from alcohol, melting at about 200°. We were unable to obtain all the nitrogen from this compound on burning with copper oxide in the usual manner. Two determinations gave 8.60 and 8.64 per cent of nitrogen, while the calculated is 10.2 per cent. In order to determine whether this peculiarity is the fault of the analytical method and whether the above compound is the benzoylurea in question, we prepared this benzoylmetachlorphenylurea by desulphurizing *benzoylmetachlorphenylthiourea*,

$$C_6H_5CONHCSNHC_6H_4Cl,$$

in regard to the structure of which there can be no question, since it was prepared from pure benzoyl rhodanide and colorless metachloraniline, the latter boiling from 229° to 231°. Here, again, we had the same difficulty on analysis; a determination gave 8.4 per cent instead of 9.6 per cent nitrogen. This material crystallizes from alcohol in colorless needles melting at 125°. On boiling the alcoholic solution of this compound with silver nitrate and a little water, a compound was obtained which crystallized in needles and melted at 200°. It was identical in every respect with the above compound obtained from the pseudourea ether. And when portions of the two samples were mixed the melting-point was not altered. It follows, therefore, that the material is the urea in question

and that this urea and thiourea do not give up all their nitrogen under the usual conditions of a nitrogen determination.

Benzoylpseudomethyl-m-nitrophenylurea, $C_6H_5CON=C(NHC_6H_4NO_2)(OCH_3)$.—After heating metanitraniline with benzoylimidomethylthiolethyl carbonate for four or five hours on the water-bath the evolution of ethyl mercaptan ceased. The oil thus obtained was treated with hydrochloric acid, whereupon it changed to a crystalline mass. This was washed with water and crystallized from alcohol, whereupon it gave

Benzoylmetanitrophenylurea, $C_6H_5CONHCONHC_6H_4NO_2$.—This is insoluble in water and chloroform and difficultly soluble in benzene and alcohol. From the latter solution it separates in the form of fine, short needles, which melt from 231°–232°. A nitrogen determination gave:

	Calculated for $C_{14}H_{11}N_3O_4$.	Found.
N	14.7	14.4

Benzoylpseudomethylpseudocumylurea, $C_6H_5CO-N=C(NHC_6H_2(CH_3)_3)(OCH_3)$, was readily formed on warming benzoylimidothiolmethyl carbonate and pseudocumidine. On cooling, the mass was treated with hydrochloric acid, whereupon methyl chloride escaped and, on washing with water and alcohol and crystallizing from chloroform, a woolly mass of very bulky, long needles was obtained. This substance melted at 207° and on analysis proved to be

Benzoylpseudocumylurea, $C_6H_5CONHCONHC_6H_2(CH_3)_3$.

	Calculated for $C_{17}H_{18}N_2O_2$.	Found.
N	9.92	9.78

Benzoylimidomethylthiolisobutyl carbonate and methylaniline reacted very slowly, giving off mercaptan. After warming on the water-bath for three days, an oil was obtained that had a beautiful purple color. It did not readily solidify with hydrochloric acid and, therefore, it was not further examined.

NEW HAVEN, CONN.,
April 30, 1900.

Contributions from the Chemical Laboratory of Bryn Mawr College.

ON SOME ISOMERIC HALOGEN COMPOUNDS OF THALLIUM, AND THE CONSTITUTION OF DOUBLE SALTS.

[FIRST PAPER.]

By Allerton S. Cushman.

Introduction.

Thallium forms simple salts with the halogens[1] of the general types TlX and TlX_3. The compounds of the type TlX resemble in color and general appearance the corresponding silver salts, and like the latter are precipitated by the halogen acids. The thallous halides are, however, appreciably soluble in water, in which respect they resemble the corresponding compounds of lead. The thallic salts of the type TlX_3 are very soluble in water, in which solvent they are more or less hydrolyzed, the solution becoming acid while the insoluble oxide, Tl_2O_3, is formed. The instability of these compounds makes it extremely difficult, if not impossible, to isolate them in pure condition. The assignment to them of the formula TlX_3 rather than the double formula Tl_2X_6 is a purely arbitrary matter resting on no experimental evidence whatever.

Thallium, in its higher state of valence, forms well-defined double salts with many other metals of the general types $TlX_3.RX$ and $TlX_3.3RX$.

In 1863 Crookes and Church[2] discovered a sesquichloride of thallium which has a formula corresponding to Tl_2Cl_3. In 1865 an extended study of the compounds of the then newly discovered element was carried on by Willne.[3] In his paper Willne sums up the reasons for believing that the compounds of the types TlX_2 and Tl_2X_3, respectively known as the tetra-

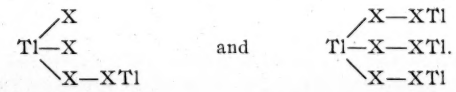
[1] As only the chlorides and bromides are considered in this paper the word halogen is used throughout as referring to chlorine and bromine only.

[2] Chem. News, **8**, 1.

[3] Ann. chim. phys., **5**, 4 (1865).

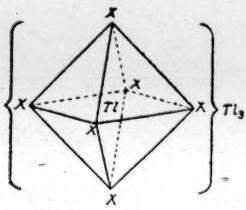
and sesqui-salts should be considered as true double salts, and be written $TlX_3.TlX$ and $TlX_3.3TlX$. In a few words the reasons may be given as follows: (1) These intermediate halogen compounds of thallium resemble in their behavior certain well-known double salts, such as $TlCl_3.CuCl$, $TlCl_3.3KCl$, $TlCl_3.3NH_4Cl$, etc. (2) When a mixture of solutions of thallous and thallic halides in the proper proportions is made the intermediate thallium compounds are obtained. (3) There are no oxides known corresponding to these intermediate salts, and, if the latter are treated with an alkali, they decompose, forming the alkaline halide, and, on the one hand, the insoluble thallic oxide, and, on the other, the thallous halide. Subsequent work has confirmed the view that these compounds are to be considered as true double salts.[1] Thallium sesquichloride has been made heretofore.[2] By heating the dry chloride, $TlCl_3$, somewhat above 100° as long as chlorine is given off, the brown liquid cools to a clear lemon-yellow mass (Lamy); also by precipitating a solution containing a mixture of thallous and thallic salts with hydrochloric acid (Willne); also by dissolving thallium or thallous chloride in aqua regia and evaporating (Crookes and Church).

It seemed that these peculiar double salts which thallium has the power of forming with itself might throw some light on the ingenious and alluring theory of Werner[3] on the constitution of double salts. Adopting the older theory of Blomstrand-Jörgensen as developed by Remsen[4], we should write the tetra- and sesqui-salts, respectively:

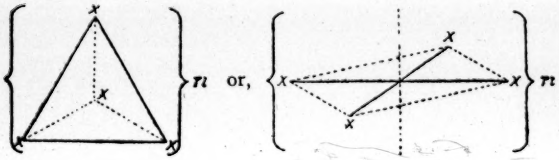


According to Werner, on the other hand, we have in the case of the sesqui-salt a dominant thallium atom at the center of an octahedron, thus:

[1] Neumann: Ann. Chem. (Liebig), **244**, 329.
[2] Watts' Dictionary (Muir and Morley), 1894.
[3] Ztschr. anorg. Chem., **3**, 267, et seq.
[4] This JOURNAL, **11**, 291.



In the case of the tetra salt we can suppose the dominant thallium atom to be at the center of a tetrahedron or we can assume a configuration of the molecule in a plane where one axis from the above type is unsaturated. Thus :

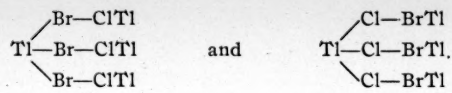


On this hypothesis we should write these compounds ordinarily $(Tl'''X_6)_3Tl'$ and $(Tl'''X_4)Tl'$. Following the assumption to its logical conclusion, we should write thallic chloride not $TlCl_3$ but $(Tl'''Cl_6)Tl'''$.

The fact that no penta halogen compounds of thallium are known to exist would seem on first thought to favor the hypothesis of Werner. According to the older theory, $TlCl_3.2TlCl$ should be quite as capable of existence as $TlCl_3.TlCl$. We must consider, however, that the tetrahedral and octahedral spatial symmetries were selected to fit the greatest number of known salts. The selection of these two types by no means exhausts the possibilities, and if compounds corresponding to a five symmetry should be obtained, they could be accounted for as well by one theory as by the other.

It seemed likely that under either of these theories it might be possible to form mixed double salts of thallium in which bromine atoms should be substituted for chlorine atoms, and *vice*

versa. Thus, for instance, we could expect isomeric forms, such as[1]



Under the older theory if these compounds were capable of existing, the isomerism would be simply a case of linkage, whereas, under Werner's theory, we should have true spatial isomerism. It was realized that a study of such isomerism and the collection of all possible evidence as to the way these compounds dissociate in solution would be of the greatest interest. Although the work is as yet uncompleted, enough has been done to justify this preliminary paper.

Preliminary Work.

At the beginning of the investigation it was noted that when chlorine is passed through water in which an excess of thallous chloride is suspended, the white color of the chloride changes gradually to lemon-yellow. If the chlorine is allowed to pass to complete saturation, the yellow compound finally disappears, owing to the formation of the exceedingly soluble thallic chloride. As the sesquichloride is to a high degree insoluble in the cold,[2] it was to be expected that the definite sesquichloride stage would be reached by this reaction before a notable quantity of the thallic salt formed and went into solution. It, therefore, seemed probable that this method would furnish a convenient way of making these double salts. A doubt remained whether the sesquichloride stage may be considered as of definite composition, or whether in passing from the thallous to the thallic state we may not obtain mixtures of variable composition.[3] The fact that the yellow compound is soluble in hot water, from which it crystallizes, on cooling, in brilliant hexagonal leaflets,

[1] The failure of R. W. Atkinson to obtain isomeric forms of $SbCl_3.3KBr$ was not known to the author until after the work here described was completed. Compare J. Chem. Soc., **43**, 289 (1883).

[2] One part in 380.1 parts water at 15°; 52.9 at 100°. Crookes, Hebberling: Ann. Chem. (Liebig), **134**, 21.

[3] Doubts on this head have been hitherto expressed. Compare Werther: J. prakt. Chem., **91**, 390.

which under a high-power microscope present every evidence of individuality, seemed to support the first assumption. Manifestly, however, complete quantitative evidence was needed of a more careful nature than any that was available in the literature. Neumann has claimed that the addition of chlorine to thallous chloride leads to the formation of the tetrachloride as well as of the sesqui-salt. As the point is important the paragraph is quoted in full :[1] "Als Ausgangsmaterial für diese Präparate diente mir anfangs Thallichlorid. Diese Verbindung ist frei von Oxydul-salze ziemlich schwer herzustellen, denn das Chlorid hat grosse Neigung in das Chlorür überzugehen was schon daraus erhellt, dass beim Lösen von Thalli-oxyd in Salzsäure immer Chlorür in nicht unbeträchtlicher Menge über dem Chlorid ensteht. Beide Salze vereinigen sich hierbei theilweise zu Doppelverbindungen von den Formeln $2TlCl.Tl_2Cl_6$ und $6TlCl.Tl_2Cl_6$. Salze in denen Tl_2Cl_6 und TlCl in Verhältniss 3 : 4 und 15 : 1 stehen, habe ich nicht erhalten, wohl aber Gemische von $2TeCl.Tl_2Cl_6$ und $6TlCl.Tl_2Cl_6$ auch mit Tl_2Cl_6. Aus solchen Gemischen, ferner aus Thallochlorid wie auch aus metallischem Thallium, erhält man die Lösung des reinen Chlorids, wenn man die genannten Stoffe in Wasser suspendirt mit Chlor behandelt."

Neumann was unable to determine the chlorine in his salts and depended on estimations of thallium alone. An electrolytic method was used and only one determination of thallium for each salt is published. Particulars beyond those quoted above are not given, and it is not apparent how the tetrachloride was made and separated from the sesqui salt. Lamy obtained the tetrachloride in the dry way by passing chlorine over fused thallous chloride, the heat being very carefully controlled. The compound was found to pass readily into the sesqui-salt. Willne[2] was never able to obtain it by any other method than that followed by Lamy, and every effort to obtain it in the wet way in this investigation has resulted in failure. The large preponderance of evidence seems to point to the conclu-

[1] Neumann : Ueber Doppelsalze von Sesquichloriden. Ann. Chem. (Liebig), **244**, 344.

[2] Willne : *Loc. cit.*

sion that the tetrachloride cannot exist in solution, the sesquichloride alone being formed.

Preparation of Pure Material.

The material which formed the basis of this investigation consisted of a mass of metallic thallium which contained as impurities a considerable quantity of lead and traces of copper and silver. In order to purify the material it was dissolved in sulphuric acid and the clear solution, after dilution, decanted from the insoluble lead sulphate. Hydrogen sulphide was then passed in and the copper and silver sulphides, together with some reddish sulpho-compound of thallium that formed, filtered out. After boiling off the excess of hydrogen sulphide this strong solution of thallous sulphate which gave no precipitate with sodic carbonate and showed with the spectroscope no alkaline impurities beyond traces of sodium, was used as the starting-point in the preparation of all the compounds hereafter described. The thallous halides, after precipitation with the pure halogen acids, were washed with cold water until quite free from sulphuric acid.

Methods of Analysis.

The quantitative determination of thallium in its compounds has presented difficulties to many experimenters, owing to the solubility of nearly all the compounds of this peculiar metal. Evidently the thallium chloroplatinate is the ideal salt through which most accurately to determine thallium, as it has been shown by Crookes to be insoluble in 15,580 parts of water at 15°. This is clearly admitted by Willne[1] as well as by Neumann,[2] but the method was discarded by both these experimenters on account of the tendency of the precipitate to pass through the filter. As carried out in this laboratory, the method presents no difficulties, and may be classed among the easiest and most rapid of accurate gravimetric operations. The hot thallium solution which, if not already in the lower state of oxidation, must be reduced by addition of sulphurous acid until the smell of sulphur di-

[1] *Loc. cit.*

[2] Ueber die quantitative Bestimmung des Thalliums. Ann. Chem. (Liebig), **244**, 349.

oxide in excess is apparent. The liquid is then carefully brought to boiling and an excess of platinic chloride added. The flask is then closed tightly with a smooth rubber stopper and the contents vigorously shaken for five minutes. After cooling, the precipitate will be found an ideal one to work with. It neither "creeps" nor clings to the glass; it is easily filtered and washed on a Gooch crucible, dries quickly, and is not hygroscopic. In drying, the precaution was taken not to allow the temperature of the oven to rise above 100°, as it has been found that the precipitate begins to decompose at a little above 100°, whereas it seems to have no tendency to retain water below 100°, and can even be brought to constant weight in a desiccator over caustic soda. This method has been used throughout this investigation, and has been found most satisfactory.

The estimation of the halogen in these compounds was complicated with difficulties. According to Neumann:[1] "Thallium hat die unangenehme Eigenschaft, bei der Bestimmung des Chlors in seinen salzsauren Salzen mit dem Silberchlorid theilweise auszufallen.[2] Da also nur mangelhafte Resultate erhalten werden konnten verzichtete ich auf die Chlorbestimmungen."

In this laboratory it was found that from a solution of a thallous halide the silver halide is as accurately precipitated as is the case with other soluble halides of monovalent metals. In the case of the thallic, as well as the intermediate double salts, we meet with an entirely different state of affairs. When silver nitrate is added to a neutral solution of one of these salts, a chocolate-brown precipitate is invariably obtained. It was found, however, that, in the presence of a sufficient quantity of nitric acid, the silver halide came down without occluding thallium. This was proved by careful spectroscopic examination of the washed precipitates as well as by abundant quantitative evidence. In analyzing these salts the following method has been found quite satisfactory: The salts are dissolved by boiling in 10 per cent nitric acid, an excess of silver nitrate is added, and the carefully stoppered flask vigor-

[1] *Loc. cit.*

[2] Compare Werther: Ztschr. anal. Chem., **3**, 1.

ously shaken. The silver halide is filtered on a Gooch crucible, washed, and weighed with the usual precautions. The composition of the dark-colored precipitate which comes down from neutral solutions will be shown later in this paper.

Preparation of Compounds.

In order to see if the sesquichloride of thallium could be obtained in a perfectly definite state, chlorine was passed through water, in which pure thallous chloride was suspended, until the white color of the chloride had completely turned to yellow. Some of this yellow compound was now removed and called Sample I(*a*). Chlorine was then passed into the residue until the yellow substance had nearly, but not quite, gone into solution. This last yellow residue was washed by decantation and called Sample I(*b*). Both samples were now twice recrystallized from water barely acidified with nitric acid. The sesqui as well as the thallic, thallium compounds are slightly hydrolyzed in water solution with separation of insoluble thallic hydroxide. The presence of nitric acid prevents this separation. The two samples prepared in this way presented precisely the same appearance, both to the eye and under a powerful microscope. When magnified 84 diameters they appeared as shining hexagonal plates of a delicate, lemon-yellow color. The analyses of these compounds are given below:

I(*a*). 1.4585 grams compound yielded 1.2132 grams AgCl.
1.2752 grams compound yielded 2.0150 grams $PtCl_4$.
$2TlCl$.

I(*b*). 1.4720 grams compound yielded 1.2303 grams AgCl.
1.2579 grams compound yielded 1.9901 grams $PtCl_4$.
$2TlCl$.

	Calculated for $TlCl_3.3TlCl$.	Found. I(*a*).	Found. II(*b*).
Tl	79.33	79.08	79.23
Cl	20.67	20.56	20.67
	100.00	99.64	99.90

These analyses show that these samples are essentially the same.

In order to study the reaction which takes place when sil-

ver nitrate is added to a neutral solution of the sesquichloride, weighed quantities of the latter were dissolved in as little water as possible to avoid hydrolysis, and an excess of a solution of silver nitrate added; the analysis was then carried out in the usual way.

1.4426 grams compound yielded 1.5230 grams dark precipitate.

1.2192 grams compound yielded 1.2910 grams dark precipitate.

Calculated for 1 gram of the substance we obtain the ratios 1 : 1.054 and 1 : 1.059.

These are satisfied by the following equation:

$$2(TlCl_3.3TlCl) + 12AgNO_3 + 6H_2O = (12AgCl + Tl_2O_3.3H_2O) + 6TlNO_3 + 6HNO_3.$$

The dark precipitate is represented by the part of the equation in parenthesis. After drying and weighing we have the ratio:

$$2(TlCl_3.3TlCl) : 12AgCl + Tl_2O_3 = 2058.8 : 2177 = 1 : 1.058.$$

For thallic chloride the reaction may be written as follows:

$$2TlCl_3 + 6AgNO_3 + 6H_2O = [6AgCl + 2Tl(OH)_3] + 6HNO_3.$$

We have in these reactions an interesting case of reversible equilibrium, depending upon the mass of the nitric acid, thus:

$$2Tl(OH)_3 + 6HNO_3 \rightleftarrows 2Tl(NO_3)_3 + 6H_2O.$$

Considered in the light of Werner's hypothesis these reactions are of interest. If we are to write the sesqui and thallic compounds, respectively, as $(Tl'''Cl_6)3Tl'$ and $(Tl'''Cl_6)Tl'''$, we should not expect chlorine ions to be present in solution, and the fact that both salts give instantaneous precipitates with silver nitrate would seem to be opposed to Werner's theory. On the other hand, it is probable that there would be a continual tendency for the halogen atoms in the complex nucleus, to be substituted by hydroxyls as is shown by the readiness with which these substances hydrolyze in solution. In view of the delicate equilibrium which determines this secondary dissociation, it does not seem improba-

ble that the addition of silver nitrate solution with its strongly positive silver ions would disturb the equilibrium and start the reaction which then proceeds rapidly to completion. On this assumption we should write the reaction as follows :

$$(Tl'''Cl_6)Tl''' + 6AgNO_3 + 6H_2O = (Tl'''(OH)_6)Tl''' + 6AgCl + 6H_2O.$$

Similarly, the reversible reaction becomes :

$$(Tl'''(OH)_6)Tl''' + 6HNO_3 \rightleftarrows (Tl'''(NO_3)_6)Tl''' + 6H_2O.$$

We have here a case of the octahedral spatial symmetry, and the direction of the reaction is conditioned under the Mass Law by the power of the hydroxyl and nitroxyl groups, respectively, to occupy the points of symmetry. Although what is here given extends the theory of Werner to include simple as well as so-called double salts, it is not advanced as a speculation, but as a logical result of the application of Werner's hypothesis to these reactions.

Preparation of the Tetra- and Sesquibromides.

These compounds were first prepared by Willne.[1] When thallous bromide suspended in very little water is treated with bromine, a yellow compound is formed, which dissolves on heating, and crystallizes on cooling in beautiful, minute, yellow needles which, under the microscope, appear as elongated quadratic prisms. On dampening the yellow crystals with water, they immediately assume a brilliant, scarlet hue. On dissolving in water and recrystallizing, dark-red crystals appear in the form of small, hexagonal plates. According to Willne's analyses, confirmed in this laboratory, the yellow needles are the tetrabromide, and the red, hexagonal crystals the sesquibromide. Throughout the study of these compounds it has been noticed that the tetra-salts crystallize in square prisms, whereas the sesqui-salts invariably appear in hexagonal forms.

The reaction that takes place in the presence of water can be written :

$$3(TlBr_3.TlBr) = TlBr_3.3TlBr + 2TlBr_3.$$

[1] *Loc. cit.*

According to Werner we may write:

$$3(Tl'''Br_4)Tl' = (Tl'''Br_6)3Tl' + (Tl'''Br_6)Tl'''.$$

It is only necessary to assume that in the presence of water the tendency of these thallium compounds is to assume the octahedral symmetry rather than the unsaturated configuration with the four bromine atoms in a plane, and the above reaction represents the only possible rearrangement. This would also account for the fact that in the case of the chlorine compound, the more active chlorine atoms do not permit the formation of a tetra salt in the wet way.

Isomeric Double Salts.

Since the treatment of thallous chloride with thallic chloride leads to the formation of a double salt, $TlCl_3.3TlCl$, it seemed possible that the treatment of thallous bromide with thallic chloride would lead to $TlCl_3.3TlBr$, while on the other hand the treatment of thallous chloride with thallic bromide would lead to the isomeric compound $TlBr_3.3TlCl$. In the first place, however, it seemed desirable to study the reaction of bromine on moist thallous chloride. Pure bromine was shaken up with thallous chloride in the presence of water until the white color of the thallous salt had changed to orange-yellow. The orange-colored substance was washed by decantation with cold water, and finally dissolved in boiling water barely acidified with nitric acid. On cooling, dark, orange-colored, hexagonal plates separated. These crystals were similar in form, but coarser and of a much darker color than the sesquichloride compound already described. After two recrystallizations, the compound was washed, dried, and prepared for analysis.

It is apparent that we have here an analytical problem of some difficulty. Theoretically, we should expect the formation of the compound, $TlClBr_2.3TlCl$. If the silver halides are precipitated together and the thallium separately determined, data are obtained from which, by indirect methods, the full percentage composition of the compound can be calculated. Only sufficient data will be inserted here to show that the compound really corresponded to the formula given above.

I. 1.1466 grams compound yielded 0.9703 gram silver halide.

II. 1.2203 grams compound yielded 1.0270 grams silver halide.

I. 1.0290 grams compound yielded 1.4998 grams $PtCl_4$. $2TlCl$.

II. 1.3545 grams compound yielded 1.9745 grams $PtCl_4$. $2TlCl$.

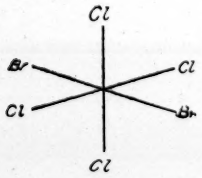
	Calculated for $TlClBr_2.3TlCl$.	Found. I.	II.
Halogen	26.99	26.90	26.76
Th	73.01	72.91	72.96
	100.00	99.81	99.72

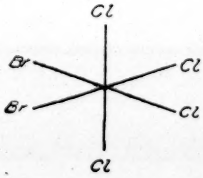
Calculating by the method of "indirect analysis" we have from I.

	Calculated.	Found.
Cl	12.67	12.50
Br	14.32	14.40
Tl	73.01	72.91
	100.00	99.81

The theoretical composition of this double salt is thus shown to be the true one. Working by analogous methods, it should be possible to form $TlCl_2Br.3TlBr$ as well as $TlCl_2Br.3TlCl$ and $TlBr_2Cl.3TlBr$. None of these compounds has as yet been made. As they would not be isomeric with each other, their study has been reserved for a future occasion.

Writing the compound $TlClBr_2.3TlCl$ according to Werner's hypothesis, we have $\left(Tl'''\frac{Cl_4}{Br_2}\right)3Tl'$. It is at once apparent that too spatial isomers are theoretically possible, as represented in the following diagrams:

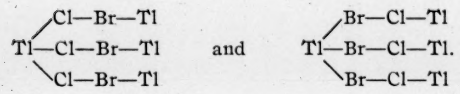




Compound No. I, of the two whose analyses are given above was made as described, by treating thallous chloride with bromine. Compound No. II was made by treating more thallous chloride suspended in water with the decanted mother-liquor from I. The reaction in the latter case went on in more dilute solution and away from the influence of free bromine. Compound No. I had an orange-yellow color. Compound No. II had a lemon-yellow color, and these separate colors were held through two recrystallizations from dilute nitric acid. The exciting question arose as to the possible isomerism of these two preparations. Every effort was made to get light on the subject, but without success. Mixtures of the two samples were made and subjected to fractional crystallization, but medium-colored crystals were obtained at each end of the fractionation. The melting-points seemed to be the same. Under the microscope the crystal forms were identical, only the shade of color being different. If these compounds are indeed isomeric, they resemble each other so closely in physical characteristics that it is impossible to distinguish them from each other. On the other hand, it is possible that the different shades of color have nothing to do with isomerism, but are due to crystal aggregation or minute traces of impurity in one case or the other. Further work is needed to decide this question.

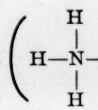
Trichlorbromides and Tribromchlorides.

When thallous bromide, suspended in hot water, is treated with a dilute solution of thallic chloride, an orange-colored compound is formed which can be dissolved by boiling. On cooling, orange-colored, hexagonal plates are deposited which resemble in general appearance Compound No. I, described above. On the other hand, when thallous chloride is suspended in a considerable quantity of hot water and treated with a hot solution of thallic bromide, a dark, blood-red compound is formed which dissolves on boiling, and, on rapid cooling, crystallizes out in beautiful, blood-red, hexagonal crystals. Written according to the older theory, these compounds should be respectively :



In these compounds we have a case of true isomerism which can be accounted for by either of the theories for the constitution of double salts under discussion. The orange isomer is very stable and can be crystallized out of water unchanged; the red isomer, on the other hand, is very unstable and is easily decomposed by water, and even by alcohol and ether. It can, however, be recrystallized unchanged out of its own mother-liquor, even after the mother-liquor has been considerably diluted. In working with this compound, a very curious example of equilibrium was noticed. As the mother-liquor is gradually diluted, a point is reached where the clear, boiling liquid, on being allowed to cool, slowly deposits a buff-colored precipitate which has the appearance of a thallous compound whose color is modified by occlusion of some sesqui salt. If, however, the boiling liquid is cooled suddenly by plunging the flask into cold water, the blood-red crystals are deposited without a sign of decomposition.

From these facts it appears that, on solution, the salt $TlBr_3.3TlCl$ dissociates into $TlBr_3$ and $3TlCl$, and that the compound that will appear on cooling is conditioned by an equilibrium depending on the temperature and the solubility of the products of the thallous salt and the double salt, respectively. On the other hand, if $TlBr_3$ and $TlCl$ exist in solution, and these compounds are in turn dissociated so that halogen ions exist, it is difficult to see why both isomers, on recrystallization, retain their characteristic individuality instead of, at least in part, passing into each other. Undoubtedly we have here a problem of great theoretical interest, though one which presents great difficulties. On first thought, the facts as stated do not seem to find any explanation under the theory of Werner, but it is possible that a condition of affairs which exists at a certain temperature and state of equilibrium is quite different at higher temperatures. In this connection it can be said that ammonium chloride can

be written on the tetrahedral type as  Cl only at a certain equilibrium, conditioned by the temperature. The fact that above a certain temperature we have (NH_3)(HCl) does not effect our belief in NH_4Cl. All the phenomena observed in this investigation point to the conclusion that the double salts do not exist in solution above certain definite temperatures. This point will be taken up again later on. Before proceeding it will be necessary to insert a sufficient amount of the analytical data obtained, to prove the composition and isomerism of these salts. There was no difficulty in preparing the orange compound for analysis, the red compound could only be washed with carbon disulphide, and it was impossible to free it entirely from its own mother-liquor.

Analysis of Orange Compound.

1.1812 grams compound yielded 1.0108 grams silver halide.
0.8969 gram compound yielded 1.2570 grams $PtCl_4.2TlCl$.

Analysis of Red Compound.

0.9515 gram compound yielded 0.8210 gram silver halide.
1.0098 grams compound yielded 1.4139 grams $PtCl_4.2TlCl$.

	Orange compound.		Red compound.	
	Calculated.	Found.	Calculated.	Found.
Cl	9.15	9.19	9.15	9.50
Br	20.63	20.59	20.63	20.24
Tl	70.22	70.14	70.22	70.07
	100.00	99.92	100.00	99.81

Since these compounds appear to be isomeric, it seemed likely that, by varying the equilibrium, some means might be found to pass directly from one to the other. If the orange compound, $TlCl_3.3TlBr$, is treated with an excess of thallic chloride, $TlCl_3$, the orange color gradually turns to a lemon-yellow and, on recrystallization, the sesquichloride, $TlCl_3.3TlCl$, is obtained. This was proved by several concordant

analyses of the lemon-yellow compound. On the other hand, if the orange compound is treated with a strong solution of thallic bromide, $TlBr_3$, long, yellow needles are obtained which, when treated with water and recrystallized, yield dark-red crystals of a sesqui-compound.

On analysis, as given below, the long, yellow needles correspond to the formula $TlBr_3.TlCl$. The change which takes place in passing from the orange to the red compound is indicated by the following reactions:

$$TlCl_3.3TlBr + TlCl_3 \rightarrow TlCl_3.3TlCl + TlBr_3;$$

$$\underset{\text{Orange.}}{TlCl_3.3TlBr} + 3TlBr_3 \rightarrow 3TlBr_3.TlBr + TlCl_3;$$

$$3TlBr_3.TlBr + TlCl_3 \rightarrow 3TlBr_3.TlCl + TlBr_3;$$

$$3TlBr_3.TlCl + (H_2O) \rightarrow \underset{\text{Red.}}{TlBr_3.3TlCl} + 2TlBr_3.$$

In the process of making the red compound by treating thallous chloride with thallic bromide, it was found possible by varying the dilution to obtain directly either yellow needles, the orange compound, or the red compound. At a certain definite point in the equilibrium, the hot solution, on cooling, may begin to deposit the orange compound. As this salt continues to settle out of the solution, the relative amount of thallic bromide present is constantly increasing, until at a certain point in the equilibrium, suddenly the long, yellow needles are seen to be forming on top of the orange, hexagonal plates, and the reaction then continues until not a vestige of the orange compound remains. This curious and interesting phenomenon has been observed over and over again in this laboratory, and it has even been found possible to adjust the equilibrium so delicately that, if the solution is suddenly cooled, the orange compound will be deposited, whereas, if gradually cooled, only the yellow needles of the tetra compound are obtained.

A question that naturally arises and one that every effort has been made to answer, is whether indeed the yellow needles correspond to the formula $TlBr_3.TlCl$ and are not in part or entirely $TlBr_3.TlBr$. In the latter case it might be doubted whether the red compound was in truth isomeric with the orange compound, but was not rather the sesquibromide,

a mixture of the latter with the orange compound. The final appeal must be to as careful quantitative analysis as is possible under the circumstances, but, first of all, qualitative evidence was sought. Some of the yellow needles were powdered together with potassium bichromate and the mixture heated with strong sulphuric acid. The vapor from this reaction, when passed through dilute ammonia, invariably gave a slight amount of yellow ammonium chromate. Samples of the true tetrabromide gave no ammonium chromate when treated in exactly the same way.

The foregoing considerations will make it apparent that the preparation and analysis of the tetrahalogen compound in question presents many difficulties. The crystals cannot be washed except with carbon disulphide, and it is therefore difficult to obtain them free from the mother-liquor. Determination of the halogen content does not aid in distinguishing between $TlBr_3.TlBr$ and $TlBr_3.TlCl$ as the analytical data fit either salt equally well. The only recourse was to the determination of the thallium, but, even in this case, it must be remembered that, as the two compounds are isomorphous, the preparation of $TlBr_3.TlCl$ quite free from $TlBr_3.TlBr$ must be a matter of difficulty, if it is not quite impossible. A large number of analyses of the yellow needles were made. Four of these, including the two worst and the two best, are tabulated below:

No. of analysis.	Weight substance taken.	Weight $PtCl_4.2TlCl$ found.	Thallium. Per cent.
6	1.0006	1.1812	59.07
4	1.0016	1.1880	59.36
3	1.0234	1.2199	59.67
2	0.7658	0.9140	59.71
		Average,	59.45

The theoretical percentage composition of the two salts is as follows:

	$TlBr_3.TlCl$.	$TlBr_3.TlBr$.
Tl	59.70	56.06
Halogen	40.30	43.94
	100.00	100.00

From the foregoing considerations it seemed that the isomerism of the orange and red compounds might be safely assumed, but it remained to be seen if any further light could be thrown on the question of their constitution. In order to get an idea of the way these compounds primarily dissociate, crystals of the orange and of the red substances were sealed up separately in stout glass tubes under their own mother-liquors, and then gradually heated in a sulphuric-acid bath. At about 100° a change in color was noticed, and, gradually, as the temperature rose, white precipitates resembling the thallous halides alone remained in the tubes. On cooling again, the double salts re-formed in well-defined crystals until finally no sign of the white thallous salt was left. It was apparent that above a certain temperature the double salts did not exist.

Physical Measurements.

It was hoped that a study of the electrical conductivity of the thallium halides in solution might shed some light on the constitution of the double salts. Unfortunately, both the thallic and the sesquithallium compounds are hydrolyzed to a certain extent in solution. While this fact prevents any accurate measurements of the conductivity due purely to the ionization of the salts, nevertheless, results can be obtained which are of value. The measurements were made by the usual Kohlrausch method in a cell of the Arrhenius type. The thermostat was kept at 25°, and all the usual precautions were taken to make the observations as accurate as possible. The conductivity of solutions of thallous chloride and thallous bromide were first measured. The limit of solubility of thallous bromide at 25° is at about one molecular weight in 250 liters, so that the first observation in the case of the latter salt is of doubtful value. μ^1 and μ^2 are calculated from measurements of two separate and independent solutions:

	TlCl.		TlBr.	
v.	μ^1.	μ^2.	μ^1.	μ^2.
62.5	128.5	129.1	....	....
125	133.9	133.9	....	....
250	136.8	137.1	132.3(?)	137.0(?)
500	139.4	139.3	147.0	148.4
1000	145.5	143.2	149.2	150.0
2000	146.2	145.0	150.1	151.0

The solution of thallous bromide at the dilution 250 was now oxidized with pure bromine and 100 cc. of this oxidized solution boiled until all excess of bromine was driven off. The solution was made up to 100 cc. again with pure water, and the conductivity measured. The fact that hydrolysis had taken place was shown by a very slight brownish tinge of the solution and a faint acid reaction to indicators. The results, however, are none the less interesting. From the figures tabulated below we see that on oxidizing thallous bromide to thallic bromide the conductivity drops to a surprising extent, especially when the calculations are based on the reaction,

$$TlBr + Br_2 = TlBr_3.$$

v.	Taken as $TlBr_3$. μ.	Taken as $(Tl'''Br_6)Tl'''$. μ.
250	61.6	123.2
500	78.8	157.6
1000	103.6	207.2
2000	141.3	282.6

As part of the observed conductivity is due to the slight amount of hydrobromic acid formed by hydrolysis, we have to conclude, on the basis of the first assumption, that $TlBr_3$ is very slightly dissociated, if at all. On the other hand, when the calculation is based on the double formula, under Werner's theory we have two trivalent ions, $(\overline{Tl'''Br_6})$ and $\overset{+}{Tl'''}$.

After each dilution more hydrolysis takes place and the minimum tone in the telephone receiver requires a constant move to the right of the sliding contact on the bridge wire. A constant position is, however, soon reached for each dilution. It was noticed in the course of this investigation that the solution of thallic bromide, after an interval of several weeks, during which it had stood in a glass-stoppered flask in the laboratory, had a much smaller conductivity than when first measured. This change was accompanied by an almost complete disappearance of the acidity as shown by indicators. The results are given in the following table :

	$TlBr_3$ (at once).	$TlBr_3$ after three weeks.	$TlBr_3$ after eight weeks.
v.	μ.	μ.	μ.
250	61.6	46.2	46.7
500	78.8	53.9	54.2
1000	103.6	64.7	65.1
2000	141.3	92.6	92.7

The reason for this change is not quite clear and is worthy of further investigation. It is possible that the hydrobromic acid under the influence of light, may be oxidized, but in that case it is hard to understand why further hydrolysis does not take place. The thallous chloride solution was oxidized with bromine in the same way as the thallous bromide, with the following results:

Taken as $TlClBr_2$.		Taken as $\left(Tl'''\frac{Cl_2}{Br_4}\right)Tl'$.
v.	μ.	μ.
250	71.1	142.2
500	104.0	208.0
1000	136.2	272.4
2000	188.2	376.4

Conclusion.

In summing up the evidence so far collected on the constitution of these double salts, it must be admitted that the question is still unsettled. The fact that these compounds are manifestly and easily dissociated into thallous and thallic compounds by heating in their own mother-liquors as described, would seem to argue against the theory of Werner. Again, the fact that silver nitrate produces immediate and complete precipitation in the cold, and that platinic chloride forms with them precipitates of thallium chloroplatinate, the thallic portion remaining in solution, points in the same direction. On the other hand, as has been stated, some of the evidence would seem to point in the other direction. The results of the conductivity measurements, as far as they have gone, appear to find a more rational explanation under the theory of Werner than under the old linkage theory. Finally, it may once more be pointed out that if $TlBr_3$ and $TlCl_3$ exist, and are even to the slightest degree dissociated in solution, there is no reason why the isomeric compounds $TlBr_3.3TlCl$

and $TlCl_3.3TlBr$ should preserve their identity through successive crystallizations.

In concluding this first paper on this subject the author wishes to express his indebtedness to his colleague, Dr. E. P. Kohler, for many valuable suggestions. For the large amount of material from which the thallium was obtained the author has to thank Hamilton Emmons, Esq., of Leamington, England.

May 15, 1900.

A MULTIPLE FAT EXTRACTOR.

By Charles L. Penny.

The chief object of the device and method described below is so to expedite the determination of fat in milk and its products as to make accurate gravimetric determinations economically possible in competition with the speedy volumetric methods now in use. This could hardly be accomplished if it were required to determine fat gravimetrically within the few minutes that the latter methods require. But when many samples are to be analyzed, if a large enough number may be worked simultaneously, the average time for each may be very short. This, then, is what is attempted; *viz.*, to extract almost any number of samples at the same time and in a single piece of apparatus, with only so much individual time spent on each as may suffice to measure the substance and to weigh the product.

The apparatus devised to this end differs in its principle of action little, if at all, from the well-known Soxhlet extractor. Its sole peculiarity is such an arrangement of parts as admits any number of samples at the same time and under a single operation to the action of the same extracting liquid. This is attained by the use of a single common chamber for all of the samples, in which they are held in shallow capsules placed parallel and close together. This chamber consists of a brass cylinder two and one-half inches in diameter and of such length as the number of simultaneous extractions may require; each half inch in length, approximately, admits a separate sample. The form described below is thirty inches long and

admits simultaneously fifty-one samples. The weight of the extract is determined by difference.

Besides the cylinder which contains the samples there are needed devices for vaporizing the extracting liquid, for condensing it and returning it condensed to the cylinder, and for siphoning from the cylinder, after the manner of the common siphon extractors. The only complication of parts beyond those used with simple extractors is caused by the large quantity of extractive liquid needed for work on a large scale. The cylinder just described contains about 2400 cc.; to vaporize and condense speedily this quantity of liquid requires not only much larger parts in the apparatus but also a more complicated arrangement of them.

Fig. 1 shows the essential parts of the apparatus and their arrangement: a complete front view on the left and a partial side view on the right. The chamber or cylinder which contains the samples is shown at C; the boiler at B, in this case fitted with steam coils at S to obviate the use of flame with so large a quantity of inflammable liquid; the condensing coils are shown above at I, and Y, their surrounding water jackets being omitted from the sketch; each has a separate water jacket, that of the smaller coil which is really placed inside of the larger, receives the cold water first. The vapor of the extracting liquid passes from the boiler by the tube N upward into the large coil, by which it is condensed; a portion of the condensation returns reflux into the annular space between the outer tube D and the inner tube I; the remaining portion, frequently the greater, is blown by the force of the incoming vapor over into the small coil from which it returns downward through G into the annular space just mentioned. Communication with the external air is at V; the vessel A allows the air to escape without the expulsion of the liquid with it. Doubtless a single large ball condenser might serve the pupose of the two coils here used, but with a coil it was found impossible to return all of the condensation reflux against the large quantity of ascending vapor. The condensations having returned to the annular space are heated by the ascending vapor in the inner tube I and, thus heated, flow through F into the cylinder C at its front end,

next to W in the side view. The siphon tube leaves the cylinder at the opposite end next to T, and passing underneath the length of the cylinder returns to the boiler as shown. The cylinder is not quite horizontal, the end T being a trifle lower. Equal vapor-pressure in boiler and cylinder, without

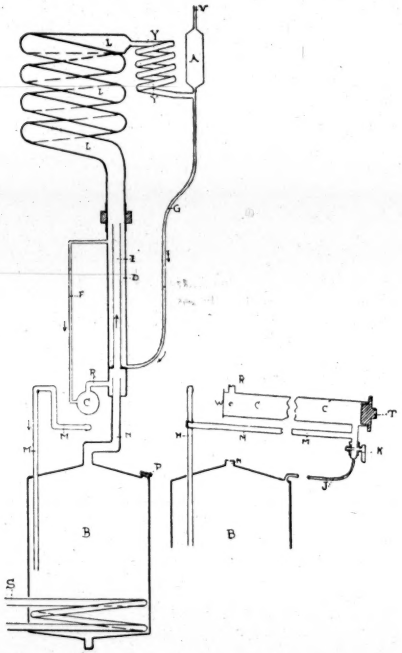


Fig. 1.

which the siphon would not work, is secured through the tube R as shown. During the extraction the cock K remains closed; afterward and previously to the removal of the cap T the former is opened to drain the liquid back into the boiler. The front of the cylinder at W is closed with mica to allow the operator to watch the process; the opposite end is closed

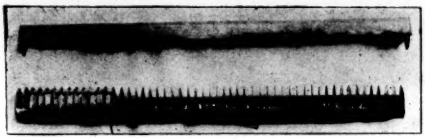


Fig. 2.

with a screw cap fitted with a leathern gasket. The parts of the apparatus are copper and brass, except the coils which are of lead for the steam, and block-tin for the condensers.

The samples to be extracted, which for the present may be supposed to be either milk, cream, skim-milk or butter, are treated after the general method of difference analysis. About 5 grams of the substance is weighed or measured into a tin-foil capsule two inches in diameter and three-eighths of an inch deep; such as are used for capping salt-mouth bottles serve admirably and are so cheap that they may with economy be thrown away after a single use. These capsules are previously charged with an absorbent such as sand or asbestos. If, in the case of milk analyses, total solids are desired, the capsule with the absorbent must, of course, be weighed previously to the addition of the milk; if the fat only is desired, this weighing is unnecessary.

The capsules with their samples are dried in the usual way and weighed. Thus the substance ready for extraction is in the form of a disk two inches in diameter and about three-sixteenths of an inch thick, securely adherent to the tin capsule but, on account of its thin cross-section, well exposed to the action of the extracting liquid and, with a proper absorbent, exceedingly permeable. The capsules are then placed in the semicircular rack shown in Fig. 2, and covered with the loose-fitting semicircular cover also shown. The rack is introduced into the cylinder of the extractor so that the crevices between the rack and its cover are in the vertical plane, an arrangement that permits the extracting liquid to surround the capsules, and to be drained off completely by the siphon action. After the cylinder is closed with the screw cap, and the cock, K, Fig. 1, also closed, the extraction is started by the admission of steam to the steam-coils at the bottom of the boiler, or by the application of some other source of heat. When the extraction is complete, the heat is shut off, the cock K is opened, and the capsules are removed. The latter are dried again and weighed, the difference being the fat.

As to the choice of absorbents, in the case of whole milk or skim-milk, in some respects asbestos is preferable, in others

coarse sand. The asbestos is much lighter and much more quickly weighed, but it is also hygroscopic. If total solids are to be determined, the capsules containing asbestos require previous drying, and weighing from desiccators. Sand, while it is heavier and slower in the weighing, is of constant weight in the air. The tin capsules mentioned above, two inches by three-eighths, weigh on an average about 7 grams. To absorb properly 5 cc. of milk, from 12 to 14 grams of sand are required while hardly more than 2 or 3 grams of asbestos. In the case of cream, and, of course, in the case of butter, sand can not possibly be used; something fibrous like asbestos is necessary in order that it may remain in the capsule. Fine powders, like precipitated carbonate of lime, are almost impervious to the extracting liquid, while asbestos, and, still more, coarse sand leave little to be desired in this respect. Paper such as is used in the Adams method would be an excellent absorbent, but doubtless its hygroscopic quality and inconstancy in weight would make it impracticable for a difference method. Glass-wool can be made to serve as a good absorbent, but it is both expensive and difficult to fit properly into the capsules on account of its elasticity. Coarse sand is the easiest to prepare and the cheapest; in proper proportion to the milk it is as satisfactory as anything that could be used.

As the capsules are placed in the extractor with their axes parallel to that of the cylinder, in other words as they stand almost vertically on edge, without a covering of filter-paper, it is clear that nothing loose enough to fall out, and so to be lost, is admissible. Sand in the proportion of about two and one-half times the weight of milk forms a firm, compact cake with the dried milk, such as admits of inversion of the capsule without the slightest chance of loss. Too much sand, of course, might leave some loose grains that would be washed away by the solvent, and thus incorrect results would be obtained. This question, however, in practice causes no difficulty whatever in the use of sand; if it be roughly measured into the capsules, a perfectly firm cake is obtained that will, with proper treatment, lose nothing mechanically during the extraction. Out of hundreds of tests with sand

there has never been a trace of mechanical loss, except where the sand cake was accidentally broken by an ill-fitting rack. Such cases, of course, would be instantly recognized and, with a proper size of rack and capsule, would never occur. Cream (and, of course, still more butter) forms too friable a cake to bind the sand, hence for such samples a fibrous absorbent, like asbestos or glass-wool, must be used. Asbestos forms with milk so firm a mat that the capsule may be dropped upon the floor and deeply indented without a particle of loss in weight. In fact very fair results may be had without any absorbent. If the milk, not more than 5 cc., be dried in the capsule without an absorbent, it may be extracted with very little danger of loss and with a fair degree of accuracy, though the extraction may be slower and a trifle less complete. Milk thus dried forms a rather brittle shell or hard skin that might well be expected to suffer certain loss from the mechanical action of the extracting liquid; yet with but ordinary care this loss does not occur, so that it would be entirely possible, though perhaps not advisable, to dispense with all absorbents.

For the purpose of milk analysis "petroleum ether" seems to have decided chemical advantages over ether, aside from its relatively low cost. The "petroleum ether" will boil at a considerably higher temperature than ether, and this, if it is below 100°, must be considered an advantage. The temperature of the interior of the boiler usually varies from 75° to 85° C. and the cylinder containing the samples is a few degrees cooler. The high temperature at which the solvent acts must hasten considerably its action. This, combined with the remarkable penetrating power of petroleum, makes it a solvent of the greatest efficiency. The time of complete extraction when sand is used as an absorbent may be in some cases as short as an hour, though usually a longer time is required. With asbestos several hours are usually necessary. As a large number of samples may be worked at one time, there is no object in unduly hastening the extraction; after six hours, however, it may be regarded as complete and, as this work may easily be effected during the night by means of a steam-heating plant, the particular duration is of little moment.

Suffice it to say, that probably after six hours the most prolonged extraction would fail to remove anything. In view of the fact that fifty, or with quite practicable arrangements, a hundred or more extractions might be made simultaneously, it would seem that the time of making a single gravimetric determination of fat is but little more than is required to make two weighings. Where the total solids of milk are determined a single additional weighing gives the fat. The time spent in drying and extracting may seem to be considerable if only a few samples are to be analyzed, but with large numbers this time is greatly reduced, and the automatic action of the device leaves the analyst free except during the transfer and weighing of his samples.

"Petroleum ether" as a partitive solvent seems to be far sharper in its lines of division than ether. It is well known that it is difficult to extract with ether to the point of an absolutely insoluble residue. Even blank trials of an ether-extracting apparatus that is fitted with corks usually show something soluble at each repetition. On the contrary, the milk residues, after a few hours' extraction with "petroleum ether," failed to lose anything appreciable by subsequent extraction. In other words, the division between "petroleum extract" and the residue is much more exact than in the case of "ether extract." This fact is probably due chiefly if not wholly to the great difficulty in drying ether and in keeping it dry, and also in drying the substance to be extracted. Only with extreme precaution can absolutely dry ether and an absolutely dry substance (for the latter is indispensable to the former) be maintained. "Petroleum ether," on the other hand, seems to be unaffected by moisture. Capsules containing extracted milk residues were treated with from 0.17 to 0.18 gram of water and thus moist were extracted without appreciable loss of weight; they were furthermore exposed to the open air on a damp day for a number of hours, and thus extracted without any appreciable change in the dry weight. The objection usually made to "petroleum ether" that it is not of definite composition would seem to apply with even more force to ether, which, as it is generally used, is itself a mixture of ether with a small but variable amount of water;

especially is this of moment in the extraction of milk and its products, which contain so much non-fatty matter that is soluble in slightly aqueous ether.

In the work with this extraction apparatus, the lighter portion of "stove gasoline" was used in place of the more costly "petroleum spirit" as it is called. The gasoline gives off at steam heat about one-half of its volume, the heavier residue remaining behind useless for this purpose. Yet with the loss of one-half, it forms one of the cheapest reagents that can be used,—so cheap in fact that the question of cost may be left out of consideration. The results obtained by the use of this extractor compare favorably with those by the ether-sand method, and in point of concordance the former have an advantage. With a large number of repetitions the multiple extractor gives less fluctuation than the ether-sand method.

While the original application of this device was to milk and its products, it seems to promise good results and expedience in fat-estimation in other substances.

DELAWARE COLLEGE
AGRICULTURAL EXPERIMENT STATION, June, 1900.

ADLUMIA CIRRHOSA—A NEW PROTOPINE-BEARING PLANT.

BY J. O. SCHLOTTERBECK.

Adlumia cirrhosa, which is variously known as Alleghany Vine, Mountain Fringe, and Climbing Fumitory, is a delicate vine climbing by its slender young leaf stalks over high bushes in wet woods, from New England to Michigan, Eastern Kansas and southward. It is also largely cultivated in gardens because of its beautiful, finely-cut foliage. It is a member of De Candolle's *Fumariaceæ*, a family so closely related to the *Papaveraceæ* that modern systematists have agreed that it more properly occupies the position of a tribe of the latter family.

Since all plants of the *Papaveraceæ*, as far as they have been studied, are alkaloid-bearing, one would be reasonably safe in assuming that all other plants of this family contain one or more alkaloids. Indeed, it would seem strange if we should

encounter a plant of this family that would fail to respond liberally to the tests for alkaloids. This process of reasoning led me to take up the chemical study of the above-named plant.

For this investigation the plant, which is a biennial, was collected in the fall of the first year's growth from the botanical garden of the University of Michigan. The roots were dug, washed, separated from the leaves and stems, and carefully dried with the aid of artificial heat. Of the thoroughly dried root, which was ground to a No. 40 powder, 10 grams were macerated twenty-four hours in a closed flask, with 100 cc. modified Prollius fluid. About 10 cc. of the filtered fluid were then evaporated to dryness on the water-bath, and the residue taken up with several small portions of water acidulated with acetic acid. The filtrate gave abundant precipitates with Mayer's and Wagner's reagent, and with ammonia water, thus indicating the presence of alkaloids. The approximate yield was estimated gravimetrically with 25 cc. of the Prollius extract, and was found to be about 1 per cent. The leaves contained very much less.

In order to learn more of the properties of the alkaloidal substance, 100 grams of the powdered root were thoroughly moistened with ammonia water, to liberate the alkaloids from their combinations, then carefully and thoroughly dried in a current of warm air, and completely exhausted in a Soxhlet apparatus with chloroform. The percolate was subjected to distillation for the recovery of the chloroform, and the residue treated with several portions of water acidulated with acetic acid. This was done upon the water-bath in order to insure the complete extraction of the alkaloid, which is more or less mechanically held by the sticky residue. The combined extracts were cooled, filtered, placed in a separatory funnel, and made alkaline with ammonia water. A voluminous, almost white, precipitate, which assumed the character of a curd, was thrown out. This was shaken with ether, whereupon the precipitate at once went into solution. This solution was only temporary, however, for from the filtered ether solution the alkaloid began to separate almost immediately in the form of white warts or sphæro-crystals, and in a few minutes practically all of the alkaloid had separated.

For the purpose of purification the alkaloid was taken up with dilute acetic acid, reprecipitated with ammonia water, shaken with ether, rapidly separated and filtered, and set aside to crystallize. This operation was repeated until a practically constant melting-point was obtained. After recrystallizing several times, finally from acetic ether, a melting-point of 203°(uncorr.)–207°(corr.) was obtained.

This alkaloid is very insoluble in petroleum ether, practically insoluble in water and in absolute alcohol, and but slightly soluble in ether, when it is in the crystalline state. When freshly precipitated from solutions of its salts by means of ammonia water, however, it is, as shown above, temporarily very soluble in ether. Its best solvent is chloroform. Being but very slightly soluble in absolute alcohol and very soluble in chloroform, a mixture of these forms an excellent medium from which the alkaloid may be easily obtained in beautiful prismatic crystals. It possesses the peculiar property of crystallizing in two different forms; *viz.*, in warts or in single prisms of the monoclinic system. Depending usually upon change of solvents, one crystalline form can be converted into the other. Even from the same solvent as from ether, or from alcohol, both forms are produced simultaneously.

The chloroplatinate forms dark-yellow sphæro-crystals while the chloroaurate forms tufts of needle-like crystals. Concentrated sulphuric acid gives momentarily with a small quantity of the alkaloid a red color, but this is immediately followed by a deep violet. Concentrated nitric acid dissolves it in the cold without color but, upon warming, it becomes red. Erdmann's reagent turns it deep violet-blue at once.

Although sufficient quantity of the alkaloid was not at hand to make combustions, enough of its properties have been determined to make its positive identification possible. In its crystalline form, solubility in the crystalline and freshly precipitated states, melting-point, color reactions, and crystalline forms of its chloride, sulphate, chloroplatinate, and chloroaurate, it agrees exactly with the protopine which we have separated from *Bocconia cordata*,[1] and with a specimen of protopine from opium.

[1] Murrill and Schlotterbeck: Proc. A. Ph. A., 1900.

The formula as determined by Hesse[1] and by Eijkman[2] is $C_{20}H_{19}NO_5$. Selle,[3] and Koenig and Dietz[4] obtained results which agree better with the formula $C_{20}H_{17}NO_5$. In spite of this small discrepancy, which is likely to occur with different operators, we are justified in asserting that the alkaloid which these investigators have investigated is in each case protopine. The conclusion as to the identity of the alkaloid of *Adlumia cirrhosa* is based upon the very characteristic properties above mentioned and upon the fact that it is identical with the protopine which we have separated from *Bocconia cordata*.

While collecting the literature upon this subject the striking similarity of the physical properties of protopine, which is the most frequently occurring alkaloid in the *Papaveraceæ*, with those of fumarine, which is the alkaloid of most frequent occurrence in the *Fumariaceæ*, was noticed. An excellent opportunity for comparing these two bodies was offered in the study of *Bocconia* and *Adlumia* which was going on in this laboratory at the same time. A specimen of fumarine, separated from *Fumaria officinalis* by P. F. Trowbridge, was also kindly placed at the disposal of the writer for additional comparative study. The composition of the alkaloid from two of these sources was not determined because of scarcity of material, but in physical properties they agreed in every particular. Fumarine is therefore probably identical with protopine.

Protopine has been found in *Papaver somniferum*,[5] *Bocconia cordata*,[6] *Chelidonium majus*,[7] *Escholtzia californica*,[8] *Sanguinaria canadensis*,[9] *Stylophorum diphyllum*,[10] and *Adlumia cirrhosa*.

Fumarine has been reported in *Fumaria officinalis* at different times by Peschier,[11] Hannon,[12] Preuss,[13] and Reichwald.[14] Battandier[15] found it in *Glaucium corniculatum* and in six or

[1] Ann. Chem. (Liebig), Suppl., **8**, 318. [2] Rec. Trav. Chim., **3**, 182.
[3] Arch. Pharm., **228**, 441. [4] *Ibid.*, **231**, 145.
[5] Hesse: Ann. Chem. (Liebig), Suppl., **8**, 318.
[6] Eijkman: Rec. Trav. Chim., **3**, 182: Pharm. J. Trans. [3], **13**, 87; Murrill and Schlotterbeck: Proc. A. Ph. A., 1900.
[7] Selle: Arch. Pharm., **228**, 441. [8] Dankwortt: Inaug. Dissert., Erlangen, 1890.
[9] Koenig and Dietz: Arch. Pharm., **231**, 145. [10] Selle: Arch. Pharm., **228**, 96.
[11] Jsbr. Fortschr. physik. Wiss., 1832, 245. [12] *Ibid.*, 1852, 550.
[13] Ztschr. Chem. (1866), **2**, 414. [14] Russ. Ztschr. Pharm., **28**, 161.
[15] Compt. rend., **114**, 1122; **120**, 1276.

more genera of the *Fumariaceæ*. Later he isolated it from *Bocconia frutescens*.

Since fumarine was discovered and named long before its discovery in opium by Hesse, it is but proper that the name protopine be dropped.

From the above it is seen that the alkaloid in question occurs in a greater number of plants than any other known alkaloid.

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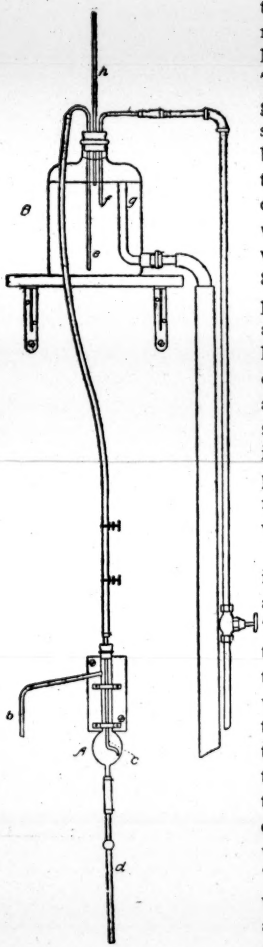
A MODIFICATION OF THE BUNSEN VACUUM-PUMP.

BY MARTIN H. ITTNER.

The laboratory vacuum-pump about to be described will, under certain conditions, be found to possess merit over the regular form of water-pump devised by Bunsen. Where there are several faucets on the same line of pipe which supplies a Bunsen pump, as is frequently the case, the flow of water through the pump is liable to fluctuate. There is a certain flow of water which produces the maximum efficiency, and when, for any reason, there is a change in the flow it is a common occurrence for some water to be drawn back into the vessel that is being exhausted. This is always annoying, and especially so when the volume of water thus sucked back is sufficient to fill the empty bottle usually placed between the vessel to be exhausted and the vacuum-pump.

Frequently, the water entering the pump contains bubbles of air which, coming at irregular intervals, cause more or less variation in the pressure within the vessel being exhausted.

The illustration shows a pump free from the most serious objections met with in the use of the Bunsen pump. It can readily be fitted up in any laboratory where a sufficient fall to the run-off water can be had. A Wurtz distilling column, *A*, 8 inches long, is selected, having an inner diameter of about 8 mm. to the tube at the bottom. A glass tube *c*, about 6 mm. in diameter and 10 inches long, is bent at one end for a short distance in the form of a helix. The opening at the end of the helix is about 3 mm. in diameter. This tube is pushed



through a singly perforated soft rubber stopper which fits the large opening of the tube *A*. The upper end of the inner glass tube is enlarged slightly so as to fit rubber connections better. The lower end of the tube *A* is connected by means of a stout piece of rubber tubing with the lead run-off pipe *d*, whose inner diameter is about 8 mm. ($\frac{5}{16}$ of an inch), the upper end of which is soldered to a short length of brass pipe having the same internal diameter. The lower end of *d* is about 37 feet below *A* and has a slight S-bend before connecting with the sewer. An iron pipe, with its unions and connections, cannot be used if a good vacuum is to be obtained.

A 4-liter aspirating bottle, *B*, is placed on a shelf about 3 feet above the bottom of the tube *A*. The upper opening of this bottle is fitted with a stopper having three perforations, through which pass the siphon tube *e*, the water feed-tube *f*, and the tube *h*. The lower opening to the bottle is fitted with a stopper through which passes the large curved overflow-tube *g*, ending within the bottle near the top. The stopper holding this tube is wired to the neck of the bottle as a precaution. The tube *h*, open at both ends, has its lower end

just below the upper end of the overflow-tube *g*. The feed-tube *f* ends about an inch below *h*. The siphon-tube *e* reaches nearly to the bottom of the bottle at one end, while the other end is connected with a rubber tube through which water may flow, passing through *c* and *d*.

When the pump is in use water is allowed to enter the bottle from the water-supply pipe *f* at such a rate that there will always be a slight overflow through *g*. All air not dissolved in the water rises to the surface and passes out of the overflow *g*. Water from the bottom of the bottle passes through *e*, and the flow may be regulated by two screw-clamps on the rubber connection. The lower of these clamps is set at the position which is found to give the most efficient flow of water and is always left there; the upper one is closed when the pump is not in use, and opened wide when in use. The water issuing at the lower end of *c* in a direction tangential to the helical end of *c* imparts a rapid rotary motion to the water in the bulb at the lower part of *A*. Whether the flow of water is slow or fast, this rotary motion always forms a vortex which carries air down the tube *d* with great rapidity. The side tube *b* is connected with the vessel to be exhausted. A volume of air equal to 1 liter can be exhausted in a few minutes until the pressure is less than 20 mm. of mercury. After the water flowing through the bottle *B* has assumed a constant temperature the vacuum remains almost perfectly constant, it being only necessary after starting the pump to see that the supply of water entering through *f* is always a little greater than that passing through *c*. The water passing through *A* does not come near the tube *b*, and there is no chance whatever of its entering *b* if the bottle *B* is kept full of water, and if ordinary care is used.

The apparatus has been found especially well adapted to distillation *in vacuo*, as a very good vacuum is easily obtained and maintained throughout the whole process with scarcely a perceptible variation in the pressure indicated by the manometer.

JERSEY CITY, May 2, 1900.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF SILVER.[1]

By Launcelot W. Andrews.

The chief volumetric methods now in use for silver determinations are those of Gay Lussac,[2] Pisani,[3] Mohr[4] and Volhard.[5]

Of these, the first, as is well known, is a process of great accuracy, applicable to acid solutions, but is tedious in execution. The second and third are only to be used in perfectly neutral solutions so that their application is extremely limited, being excluded in those cases where neutralization produces a precipitate. The method of Volhard is free from these drawbacks but is seriously interfered with by the presence of substances which impart a yellow or red color (such as cobalt salts) to the solution and for those cases in which the amount of silver is extremely small or the solution highly dilute, it lacks the sensitiveness of the methods of Gay Lussac or Pisani, probably because the reaction between sulphocyanates and ferric salts is less delicate as a test for the former than for the latter.

It has therefore appeared to the author to be a matter of some interest to devise a method applicable to acid solutions containing silver along with a variety of other metals, possessing the delicacy characteristic of the starch-iodide reaction. It is the purpose of this paper to present such a method, based upon that of Pisani.

In Pisani's method, a solution of starch iodide is run into the silver solution containing calcium carbonate in suspension.

The exact nature of the reaction which then occurs and which culminates in decolorization of the iodide of starch has not been as yet cleared up in spite of several investigations which have been published on the subject. Silver iodide is precipitated along with oxidized products, silver

[1] Presented at the New York meeting of the American Association for the Advancement of Science, June 28, 1900.

[2] G. J. Mulder: *Scheikundige verhandelingen*, 1857.

[3] Ann. des Mines [5], 10-83.

[4] Titrirmethode, 3rd ed., § 151.

[5] Ann. Chem. (Liebig), 190, 1.

iodate, hypoiodite or, possibly, silver peroxide in the latter stages of the reaction. Strict proportionality does not exist between the amount of starch iodide consumed and the silver present, although such proportionality is more nearly approached as the solution used is more dilute. The departure from proportionality for solutions between $\frac{N}{100}$ and $\frac{N}{200}$ is considerable, as the following experiments show.

In each experiment 25 cc. of a solution containing 0.7887 mg. of silver was employed and the quantity of water added was varied. The results of one set of observations are subjoined.

Expt. No.	Vol. of water added in cc.	Vol. of Pisani's sol. required. cc.	Character of end reaction.
41	None	15.70	Obscure, color dirty.
42	300	18.60	Sharper.
43	None	15.40	As in No. 41.
44	500	20.25	Sharp. Change from brownish to blue.
45	300	18.70	As in No. 42.

If the effort is made to titrate a silver solution acidified with nitric acid by one of starch iodide, a series of colors may be observed, beginning with yellow and passing through orange, brown, gray, sage-green, etc., without any turning point being clearly marked.

During these changes, the solution exhibits powerfully oxidizing properties, more marked than are shown by dilute solutions of either iodine or of iodic acid. The reaction between free iodine and solutions of silver nitrate is now under investigation at this laboratory, and the author hopes to publish definite results before long; in the meantime it will suffice to say that the following general reaction is probable, the equation being written in the sense of the electrolytic dissociation theory:

$$I_2 + \overset{+}{Ag} + \overset{-}{NO_3} = AgI + \overset{+}{I} + \overset{-}{NO_3} = AgI + INO_3.$$

Here the iodine plays a part similar to that which it holds in iodine monochloride and the—for the present—hypothetical compound INO_3 is to be regarded as the carrier of the oxidizing properties referred to above. It exerts the oxidizing action upon organic matter present (as starch) and upon any

other reducing substances such as ferrous salts, nitrous acid, or tetrathionates. It undergoes, in part, hydrolysis into HOI and nitric acid and, in part, reacts with the excess of silver nitrate, producing a reddish-brown solution precisely similar in appearance and properties to that obtained by dissolving "silver peroxide" in nitric acid,[1] and which presumably contains silver pernitrate.

In place of these complicated reactions, a simple one ensues if from the start a sufficient quantity of a feeble reducing agent is present, as ferrous salt or nitrous acid, of such character as not to react with free iodine or starch iodide. In that case a smaller quantity of the solution of iodide of starch will be required than if the titration were conducted according to Pisani in neutral solution, and the end of the reaction is marked by a sharp change from pale yellow to blue.

The reaction is shown by the equation:

$$2AgNO_3 + 2Fe(NO_3)_2 + I_2 = 2AgI + 2Fe(NO_3)_3$$

or more simply according to the dissociation theory:

$$\overset{++}{Fe} + \overset{+}{Ag} + I = AgI + \overset{+++}{Fe},$$

and, for the case in which nitrous acid is present, by

$$HNO_2 + 2AgNO_3 + I_2 + H_2O = 3HNO_3 + 2AgI;$$

or $$\overset{-}{N}O_2 + 2\overset{+}{A}g + I_2 + \overset{-}{O}H = \overset{+}{H} + \overset{-}{N}O_3 + 2AgI.$$

As might be expected from the respective equations, the reaction in the presence of ferrous salts is practically instantaneous, while that which takes place in the presence of nitrous acid is much slower, especially in very dilute solutions, owing to the slight dissociation of the water and consequent small number of hydroxyl ions that are directly involved in the reaction.

Dilute solutionsof ferrous salts, slightly acidified by strong acids will very slowly decolorize properly prepared starch iodide, with the formation of traces of ferric salts. This action can be checked by the previous addition of ferric salt. Thus, if 2 cc. of a solution of forty grams of crystallized ferrous ammonium sulphate in a liter of water be added to 100 cc. of

[1] J. Fischer: J. prakt. Chem., **33**, 237.

water containing 5 cc. of dilute nitric acid, and a few drops of N/1000 starch iodide then run in to color the liquid blue, spontaneous bleaching will ensue in about five minutes, whereas, if the iron solution also contains 40 grams of ferric ammonium sulphate (cryst.) per liter, five to eight hours will elapse before the blue disappears. That there is a condition of equilibrium between ferrous and ferric salts and iodine and iodide has been shown by Seubert and Danner[1] and by Seubert and Rohrer.[2]

In applying the facts just set forth to the development of a practical volumetric method, the slight solubility of silver sulphate must be born in mind. If the iron sulphate is added to a too concentrated silver solution and then titration with starch iodide is undertaken, silver sulphate will be thrown down with silver iodide and partly enveloped by the latter, making the end-point obscure and the results more or less inaccurate. Some of the experiments described in the following pages give evidence of this fact and also show the permissible limits of concentration.

Before describing in detail the analytical method, it will be well to say a word regarding the adjustment of apparatus and the preparation of solutions employed.

Apparatus.

All burettes and other pieces of volumetric apparatus employed in the work were carefully calibrated and the readings corrected to true cubic centimeters. The burettes were divided into 1/10 cc. with divisions sufficiently wide to permit 1/100 cc. to be estimated with an error of not more than 2/100 cc. The solution of iodide of starch in the concentrations used is almost perfectly opaque and permits very exact readings to be taken from the top of the meniscus, which method was uniformly used.[3] Pipettes and burettes were

[1] Ztschr. anorg. Chem., 5, 339-411.

[2] *Loc. cit.*, 7, 137.

[3] The use of a float is not to be recommended, according to the author's experience, for either opaque or transparent liquids. Many series of readings made with and without this device, the results being controlled by weighing the liquid delivered, have shown that the float increases instead of diminishing the probable error of a reading, provided the readings are taken in the proper way when no float is used; *i. e.*, with suitable illumination.

frequently cleaned with a strongly alkaline solution of potassium permanganate followed by hydrochloric acid, a method to be recommended in preference to that involving the use of sulphuric acid and potassium bichromate commonly employed.

Preparation of Standard N/10 Silver Solution.

Commercial "pure silver 1000 fine" was dissolved in pure nitric acid and water, heated in porcelain and filtered. An excess of the purest hydrochloric acid was added and stirring continued until the precipitated chloride had become granular. The precipitate after being thoroughly washed by decantation was reduced by digestion on the steam-bath with formaldehyde and ammonia. The silver sponge so obtained was washed with distilled water, compressed and fused in an unglazed porcelain crucible without flux, cast in an ingot mold, treated with fusing caustic potash, and finally cleaned mechanically. The N/10 solution was made up to contain 10.793 grams (corrected) of this silver per true liter. From this standard a N/100 solution was prepared directly by dilution, and for some of the experiments, other, less pure, silver solutions were standardized by comparison.

Preparation of the Starch Iodide.

The best obtainable commercial maize starch was repeatedly washed with water by decantation, strained through linen, washed with dilute hydrochloric acid, then with pure dilute caustic potash, again with hydrochloric acid, then in turn, with water, alcohol, ether, and finally alcohol, and dried at 40°. This purification is not essential, but the starch employed had been purified in this way for the purposes of a correlated research on the properties of starch iodide.

Of the prepared starch, 50 grams were ground dry with 8 or 9 grams of resublimed iodine until well incorporated and the powder stirred with 100 cc. of distilled water, sealed up in large glass tubes and heated for several hours in boiling water. Instead of heating in sealed tubes, boiling with water in a flask with reflux condenser may be equally well employed, the iodine, which at first sublimes into the condenser, being

pushed back into the liquid from time to time. The substance obtained in either way, after moderate dilution, is filtered through a "toughened" (parchmentized) filter. Solution is complete. N/20 standard solutions were made, but N/100 is as far as it is convenient to go in concentration usually. These solutions are as absolutely permanent as any volumetric solutions can be, changing in strength only by evaporation of water. By blowing a current of air through such a solution for a day or two the vapor-pressure of the iodine can be reduced to 0.005 mm., and even less, as was determined by a method to be published elsewhere.

For all titrations where an iodine solution weaker than N/20 is to be used, as in the titration of alkaline arsenites, antimonous salts, etc., iodide of starch solutions are to be preferred to those prepared in the ordinary way from potassium iodide and iodine, since the former are more permanent, give an even sharper end reaction, can be more exactly read off in the burette and avoid the difficulty of preparing a clear, permanent starch solution as indicator or the trouble of always making up a fresh one. The standard of a solution of starch iodide as regards silver is not the same as its standard toward sodium thiosulphate, since only a part (often about $\frac{2}{3}$) of its iodine is in a condition to react with reducing agents, the remainder being in a form analogous to an alkyl iodide, reactive toward silver salts but not toward thiosulphates, and the like.[1] In some experiments (referred to below) a N/10 solution was prepared (designated "Sol. A") by mixing about 600 cc. of N/50 starch iodide with about 400 cc. of ordinary decinormal iodine solution. The mixture was decinormal as regards total iodine. Such solutions can be used when larger amounts of silver are to be titrated, but I believe it to be better in such cases to precipitate the greater part of the silver with a N/10 potassium iodide solution and finish with the N/100 starch iodide, or to use a N/10 potassium bromide and then, *after filtration*, to titrate with the starch iodide. Starch iodide reacts with the chloride, bromide, cyanide, or sulphocyanate of silver, so that these salts must

[1] Compare Mylius: Ber. d. chem. Ges., **20**, 688. The statement made above is intended to apply only to iodide of starch prepared by the aid of *heat*, as described in the present paper.

always be filtered out before proceeding to the residual titration.

Auxiliary Solutions.

Iron solution C contained 40 grams ferrous ammonium sulphate and 40 grams ferric ammonium sulphate with a few cc. dilute sulphuric acid to the liter. For reasons already given, it is desirable to have solutions of ferrous and ferric salts free from sulphates to use for this method. Experiments were accordingly made with solutions obtained from iron and dilute nitric acid, containing about 28 grams of iron to the liter and were successful. Such solutions have the disadvantage of gradually becoming deep brown in consequence of the formation of basic ferric nitrate, and they contain organic matter derived from the carbon of the iron. This organic matter takes up a little iodine and therefore decolorizes starch iodide. Solutions prepared from strontium nitrate with solutions of ferrous and ferric sulphates are free from the latter objection but not entirely from the former.

Instead of ferrous solutions, those of nitrous acid may be employed as previously mentioned. They may suitably be prepared by dissolving 30 grams of sodium nitrite (free from chloride) in one liter of dilute nitric acid (13 per cent). Such a solution is designated "Sol. D" in the following tables.

Experiments on the Influence of Dilution and Degree of Acidity.

In the first series of experiments recorded below, a solution (slightly acid) of silver nitrate containing 0.7887 gram of silver was used and an empirical solution of starch iodide, of which 1 cc. = 1.639 mg. of silver designated as "sol B."

Series I.

Expt. No.	cc. Ag solution.	cc. H_2O added.	cc. dillute HNO_3 added.	cc.	cc. nitrous acid or iron solution.	cc. iodide of starch required.	Remarks.
46	25	None	....	4	Sol. D.	13.90	End reaction sharp.
47	25	250	....	20	Sol. D.	13.25	" " "
48	25	None	1	2	Fe Sol. C.	11.85	Ag_2SO_4 precipitated
49	25	"	5	2	"	11.85	" "
50	25	250	5	2	"	12.20	" "
51	25	250	5	2	"	12.17	" "
52	25	1000	5	2	"	12.65	" "
53	25	1000	20	2	"	12.67	" "
54	25	1000	20	8	"	12.63	" "
55	25	100	5	2	"	12.11	" "

Series II, 2 cc. of Iron Solution (C) Added in Each Experiment.

Expt. No.	cc. Ag solution.	cc. H_2O added.	cc. dilute HNO_3 added.	cc.	cc. Pb or Cu solution.	cc. iodide of starch required.	Remarks.
56	25	250	5	10	N/10 $Pb(NO_3)_2$	12.21	
57	25	250	5	10	"	12.18	
58	25	None	5	10	"	11.57	Ag_2SO_4 precipitated with $PbSO_4$.
59	25	25	5	10	"	11.97	Ag_2SO_4 precipitated with $PbSO_4$.
60	25	250	5	10	"	12.20	
61	25	None	5	10	"	12.02	Ferrous nitrate used instead of sulphate.
62	25	"	5	10	" (*v.* No. 58)	11.65	
63	25	250	5	10	N/10$Cu(NO_3)_2$	12.20	
64	25	None	5	10	"	11.88	Ag_2SO_4 precipitated.

Series III, Iodide "Sol. A" (See page 261), adjusted to = N/10 Silver Solution. "B" is an Arbitrary Solution of Silver Nitrate.

Expt. No.	cc "Sol. B."	cc. H_2O added.	cc. HNO_3.	cc. iron solution.	cc. "Sol. A" required.	Remarks.
65	25	150	2 conct.	8 Fe sulphates	18.27	
66	25	150	12 "	8 "	18.30	
67	25	150	2 "	2 "	18.25	Very quick titration.
68	25	None	2 "	$Fe(NO_3)_3$ from Fe	18.18	Very slow titration.
69	25	"	2 "	$FeSO_4 + Sr(NO_3)_2$	18.25	Very slow titration.
70	25	"	10 "	$FeSO_4 + Sr(NO_3)_2$	18.25	5 cc. satur'ed sol. $NaNH_4HPO_4$.
71	25	150	2 "	8 Fe sulphates	18.27	25 cc. N/10 $Pb(NO_3)_2$ sol.
72	25	150	4 "	4 Fe nitrate sol.	18.25	
73	25	None	20 dil.	$FeSO_4 + Sr(NO_3)_2$	18.21	
74	25	150	20 dil.	$FeSO_4 + Sr(NO_3)_2$	18.27	
75	25	None	20 dil.	$FeSO_4 + Sr(NO_3)_2$	18.21	
76	25	50	.....	12 cc. nitrous acid, "Sol. D"	18.15	
77	25	100	.....	10 cc. nitrous acid, "Sol. D"	18.22	
78	25	100	.....	10 cc. nitrous acid, "Sol. D"	18.25	
79	25	100	.....	5 cc. nitrous acid, "Sol. D"	18.23	
80	50	None	.....	10 cc. nitrous acid, "Sol. D"	36.36	

From these results the following conclusions may be drawn:

I. Within certain limits the amount of free nitric acid is without appreciable influence.

II. A considerable excess of iron solution is without influence.

III. For increasing dilution a very small correction is called for which amounts to 0.10 mg. of silver for each 100 cc. of solution. This correction is to be subtracted from the results directly obtained.

IV. If the solution titrated contains much more than 20 mg. of silver per 100 cc. the results are too low in consequence of precipitation of silver sulphate with the iodide. This influence also appears in experiments numbered 58, 59, 62.

The object of the second series, experiments 56 to 62 inclusive, was to show the influence of lead salts upon the titration. It is apparent that there is no influence except when in consequence of insufficient dilution the precipitate of lead sulphate carries down silver sulphate with it as is shown in numbers 58 and 62, and to a less extent in number 59, where the addition of 25 cc. of water renders the results almost normal. That these errors are really due to the sulphate and not to the lead is shown by number 61 in which the same amount of lead salt was used but no sulphate, ferrous and ferric nitrate solution being substituted for it. The titrations in the presence of copper nitrate, numbers 63, 64, show that this salt, as might be expected, is without influence on the result. The solution of lead contained 20.7 grams of the metal per liter; that of copper 63.3 grams. There was accordingly about five times as much lead present as silver or about one and a half times as much copper.

Under Series III a number of observations have been brought together upon the titration of larger amounts of silver, in more concentrated solution and under varying conditions, with the combined solution of starch, potassium iodide and iodine. The deductions to be drawn from these data, in addition to those already derived in the foregoing pages may be enumerated as follows:

I. The correction for dilution does not exceed 0.02 cc. of the N/10 solution for each 100 cc. additional water.

II. The influence of varying speed of titration is inappreciable.

III. The influence of varying amounts of free acid (above a certain minimum) or of ferrous salt, is inappreciable.

IV. The results obtained by the use of nitrous acid as a deoxidizer are not directly comparable with those obtained when the ferrous and ferric salts are used, being lower when the solution is concentrated and higher (see Experiments 46 and 47) when dilute.

The results with the iron salts are also more constant and the reaction quicker.

V. Phosphates and lead salts are without influence.

Other experiments, not necessary to detail, show that arsenates and antimonates are without influence.

On the basis thus secured it is possible to lay down a general

Method of Procedure.

The silver solution to be titrated should be acid with nitric acid but ought not to contain enough of this reagent to oxidize a ferrous salt in the cold; that is, it should contain less than five per cent of the acid, HNO_3. It must be free from mercury and from the lower oxides of arsenic and antimony, but may contain sulphurous acid.

Add a ferrous salt in such amount that at least as much iron shall be present as silver and an equal quantity of a ferric salt. An excess of the latter must be added if the original solution contained sulphurous acid. If nitrous acid is present it must first be removed by boiling.

The mixture of ferrous and ferric salts are best kept on hand in the form of sulphates which, just before use, are converted into nitrates by the addition of a moderate excess of strontium or lead nitrate solution, the last step being superfluous when the silver solution contains less than 20 mg. silver per 100 cc.

The titration is to be carried on with constant stirring and not too rapidly. Under these conditions the end reaction is never in doubt to the extent of even 0.05 cc., provided that all reagents used are perfectly free from chlorine. A subsequent bleaching of the solution in the course of an hour or two is to be disregarded. A porcelain dish is much more suitable than a beaker for the titration on account of the uniform, white background.

Applications.

The method described is obviously applicable in many ways to residual analyses, as of chlorides, cyanides, etc., and appears especially suitable to the determination of small quantities of these substances as in water analysis. The author intends to elaborate the process further, and desires to reserve the field for a reasonable time.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF IOWA, June 1, 1900.

THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK BY THE BABCOCK TEST.

By E. H. Farrington.

The Babcock test is now a standard method for the estimation of butter-fat in nearly all kinds of dairy products. It is universally used for examining whole milk, skim-milk, buttermilk, whey, and cream, and it has also been successfully applied to the determination of fat in cheese and in condensed milk containing no sugar. A large proportion of the canned condensed milk, however, is sweetened with cane-sugar, and up to the present time no satisfactory way of testing this sweetened milk has been devised. Instead of the clear fat, a black, flocculent substance separates in the neck of the test-bottles, and when carried out in the usual way it is impossible to obtain a satisfactory reading with such milk.

Many attempts have been made to obtain a clear separation of fat by using more or less acid, or acid of different strengths, but these modifications have not overcome the difficulties. The common way of determining fat by extracting the sweetened condensed milk with ether is also unreliable, so that chemists have not had any satisfactory method for estimating the fat in condensed milk to which sugar has been added.

Since it is evident that the excess of cane-sugar is responsible for this poor separation of the fat, some way of removing this sugar must be devised in order to make any method of analysis successful. This I have found can be done by a few changes in the ordinary manipulation of the Babcock test.

In order to wash out the sugar without removing any of the fat in the washings, I first had a test-bottle made with two necks. One of these is the usual graduated neck, and the other is a side tube of about the same bore and fully as long as the neck tube, but extending to the inside bottom of the test-bottle. By means of this side tube the sugar solution can be siphoned out of the test-bottle after the curd has been separated with a few drops of acid.

A number of trials with this test-bottle showed that the excess of sugar could be removed in this way and that a clear

separation of the fat is afterwards obtained by completing the test in the usual manner. It soon became evident, however, that the side-tube was superfluous, and that the whey could be poured off from the curd through the graduated neck of the test-bottle as safely as it was siphoned through the side tube. This is made possible by whirling the test-bottles in a steam-heated centrifuge at such a speed that the curd is cooked into a rather hard lump, which does not break when the whey is poured off.

A brief description of the manipulation adopted will explain the method that has proved satisfactory.

From 40–60 grams of condensed milk are weighed into a 200 cc. graduated flask; about 100 cc. of water are added, and the solution of the condensed milk effected. The flask is then filled to the mark with water, and, after mixing thoroughly, a 17.6 cc. pipette full is measured into a Babcock test-bottle. About 3 cc. of the sulphuric acid commonly used for testing milk are added, and the milk and acid mixed by shaking the bottle vigorously. The milk is curdled by the acid, and the curd and whey separated somewhat. In order to make this separation complete and to compact the curd into a firm lump, the test-bottle is whirled for about six minutes at rather a high speed (1,000 rev.) in a steam-heated turbine centrifuge.

The chamber in which the bottles are whirled ought to be heated to about 200° F. This can be done either by the turbine exhaust steam which leaks into the test-bottle chamber of some machines, or by means of a valve and pipe which will allow steam to be turned directly into the test-bottle chamber. After this first whirling, the test-bottles are taken from the centrifuge, and by being careful not to break the lump of curd, nearly all the whey or sugar solution can be poured out of the neck. Ten cc. of water are then poured into the test-bottle, and the curd is shaken up with it so as to wash out more of the sugar. Three cc. of acid are then added as before and the test-bottle whirled a second time in the centrifuge. The whey is decanted again, and this second washing removes so much of the sugar that it will not interfere with testing in the usual way. The curd remaining in the test-bottle after the second washing is shaken up with 10 cc. of

water, and to this water-emulsion of the curd the usual amount, 17.5 cc., of sulphuric acid is added and the test completed in the same way as milk is tested. The amount of fat finally obtained in the neck of the test-bottle is calculated to the weight of condensed milk taken.

Several analyses of the same sample were made using a different weight of condensed milk each time. The results, when calculated to the original substance, gave as nearly the same percentage of fat as could be expected from duplicate analyses.

Five brands of sweetened condensed milk were examined by this process, at least four determinations being made of each sample. The fat separated was clear and the final results satisfactory.

Sixty grams of the condensed milk is about the right amount to take in a 200 cc. flask, then each 17.6 cc. pipette full of this 200 cc. is equal to 5.28 grams of the sample tested. The common brands of condensed milk will give a reading from this weight of about 2 per cent on the neck of a Babcock test-bottle. The volume of fat occupied by 1 per cent on the scale of the test-bottle is equal to 0.18 gram fat, and 3 per cent would show 0.54 gram fat, which is 10.22+ per cent of the 5.28 grams condensed milk tested.

The following results were obtained with the five samples examined, each sample was tested four or more times, with a very satisfactory agreement of results in each case :

Sample No.	Weight and dilution of condensed milk tested.	Test-bottle reading.	Per cent fat in condensed milk.
1	60 grams to 200 cc.	2.4	8.00
1	29.6 " " " "	1.25	8.00
2	32.7 " " " "	1.6	10.00
3	51.6 " " " "	2.4	9.30
4	45.4 " " " "	2.3	10.35
5	65.8 " " " "	2.0	6.35

The condensed milk may be transferred to the weighed measuring flask by means of a glass funnel which reaches to the bulb of the flask, pouring the thick liquid previously mixed with a spatula directly from the tin can into the funnel through which it will run freely if the throat of the funnel is large enough.

Careful tests of the whey poured off from the test-bottles showed that no fat was lost by this decantation if the whey was clear and contained no pieces of curd.

It is essential that the curd should be cooked in the test-bottle so as to cause it to shrink into a compact lump, which does not break when the whey is poured off.

If only 20 grams condensed milk are measured into a 200 cc. flask, a difference of 0.2 per cent of fat on the neck of the test-bottle amounts to about 2 per cent fat in the original substance. It is therefore well to test a more concentrated solution of the milk than this. As stated above, about 60 grams to 200 cc. give a satisfactory solution.

DAIRY SCHOOL,
UNIVERSITY OF WISCONSIN, MADISON, WIS.,
July 24, 1900.

Contribution from the North Carolina Agricultural Experiment Station.

THE PURIFICATION OF PHLOROGLUCINOL.

BY G. S. FRAPS.

In the determination of pentosans in vegetable materials, the substance is distilled with hydrochloric acid of 1.06 sp. gr., the furfural precipitated with phloroglucinol, and the precipitate weighed.

Commercial phloroglucinol contains diresorcinol as an impurity, which is difficultly soluble in hydrochloric acid of 1.06 sp. gr. According to Kruger and Tollens,[1] small quantities of diresorcinol do not affect the determination; but Councler[2] found from 7.5 to 14.6 per cent of diresorcinol in commercial pure phloroglucinol, and concludes that it varies greatly in composition, and often contains enough diresorcinol to vitiate the results. The methods of analysis of the Association of Official Agricultural Chemists of this country, require the use of a phloroglucinol free from diresorcinol for the determination of pentosans. The bar to the use of this preparation is its great price, as it costs nearly its weight in gold.

Since the diresorcinol is difficultly soluble in hydrochloric acid of 1.06 sp. gr., and 100 cc. of the acid dissolves 0.7 gram phloroglucinol at 15° C., phloroglucinol can be purified

[1] Ztschr. angew. Chem., 1896, 40.
[2] Chem. Zeit., 1897, 2.

by dissolving it in hydrochloric acid, and allowing the diresorcinol to crystallize out. The diresorcinol which remains in solution will not affect the accuracy of the determination.

The method of purification is as follows: About 300 cc. of hydrochloric acid, 1.06 sp. gr., are heated in a beaker and 11 grams commercial phloroglucinol added in small quantities at a time, stirring constantly until it has almost entirely dissolved. Some impurities may resist solution, but it is unnecessary to dissolve them. The hot solution is poured into a sufficient quantity of the same hydrochloric acid (cold) to make the volume 1500 cc. It is allowed to stand at least over night—better several days—to allow the diresorcinol to crystallize out, and filtered immediately before using. The solution may turn yellow, but this does not interfere with its usefulness. In using it, the volume containing the required amount is added to the distillate from the pentosan.

The phloroglucinol solution prepared in this manner has been compared with phloroglucinol free from diresorcinol, and found to give as good results. Duplicate analyses of substances containing pentosans agreed as well as could be expected. On three solutions of furfural, the weights of precipitates were, using phloroglucinol:

	I. Gram.	II. Gram.	III. Gram.
Purified as above described	0.4575	0.5115	0.4647
Merck's, free from diresorcinol	0.4620	0.5124	0.4671

THE WIDE OCCURRENCE OF INDICATORS IN NATURE.

By G. S. Fraps.

In the course of some work on a black cow-pea bean, the writer's attention was attracted by the change from black to red, which took place when it came in contact with an acid. Later, in speaking to Mr. G. H. Whiting, a student, about this, he mentioned that the juice of the blackberry had the properties of an indicator. These observations led to the work about to be described. Since completing it, the writer has been informed that a lady placed some violets in ammo-

nia water to preserve them, and to her astonishment, they became green.

The results of this work show that indicators are of very common occurrence in nature. Some seventy-four kinds of colored flowers, both wild and cultivated, the leaves of five varieties of coleus, the cow-pea bean, the blackberry, mulberry, smilaxberry, strawberry, and the red beet were extracted with water or dilute alcohol, and the extract tested for indicators. In only three cases did the extract not become one color when acid and another color when alkaline. As a rule, the coloring-matter was fairly sensitive as an indicator, being changed by from less than 1 to 2 drops of tenth-normal ammonia. Some of the changes were very sharp, and many of the colors were very beautiful. In some cases the color passed through several stages in going from acid to alkaline, or the reverse.

The materials examined could be grouped in four classes:

Class I.—Extract not affected by acid or alkali.

Class II.—Extract colorless when acid, yellow when alkaline.

The flowers in this class were yellow, and the yellow coloring-matter was hardly affected by the extracting agent.

Class III.—Extract red (or a shade of red) when acid, yellow when alkaline.

Class IV.—Extract red when acid, green when alkaline.

Classes III and IV are not sharply separated, sometimes the color produced by the alkali being such that it was hard to decide whether it was yellow-green or green-yellow. Ammonia was the alkali used; often a green solution with ammonia would have been yellow with caustic soda. Most of the coloring-matters in these two classes were very sensitive. In many cases the flowers were bleached when boiled with water, and the extract nearly colorless, or quite so, but it would become colored when made acid or alkaline.

Class V.—Miscellaneous. This includes all that do not fall in the other four classes. It must be observed that in no case do the colors occur in the reverse order from those in the other classes—that is, never colorless when alkaline and yellow acid, or red when alkaline and green or yellow acid.

The colors of the coleus especially, depend on the degree of acidity of the leaf as well as on the kinds and distribution of the colors. With coleus colors there is a regular change in color from acid to alkaline, or the reverse, passing through several stages. It is easy to see that a slight change in the acidity of the sap of the leaf will affect the color and give rise to some of the manifold variations that are observed in the coleus. The same may be said of some flowers.

Methods of Examination.

Two methods were adopted for testing the color. In the one, small portions of the material were placed into two test-tubes with alcohol, a few drops of fifth-normal hydrochloric acid added to one, of tenth-normal caustic soda to the other, and the changes noted. It usually requires some time for the effect to be visible. In the second method the material was boiled in a large test-tube with about 20 cc. of water, to which a little alcohol was often added, cooled, the extract poured off, and titrated with fifth-normal acid and tenth-normal ammonia. The two methods usually gave the same results, though they were sometimes different, as was to be expected, as in the one case all of the color, soluble and insoluble, was subjected to the action of caustic soda; in the other case only the soluble part was treated with ammonia. Method 2 allowed some conclusion as to the sensitiveness of the color to be made :

Class I.—Color unaffected by acid or alkali. This includes the orange flowers of *Stylosanthus biflora*, the yellow ones of *Chrysogonum Virginianum*, and the leaves of a smooth, red variety of coleus. Three materials not containing indicators were found out of 81 examined.

Class II.—The flowers in this class give a colorless extract which becomes yellow when made alkaline.

The color is moderately sensitive. All of the flowers but one—the white petals of the wild daisy—are yellow or orange. Yellow is a color which cannot be extracted by boiling water. In some cases it goes into solution with the tenth-normal caustic soda.

This class comprises 10; stamens of begonia and *Solonum*

Carolinaense; petals of canna, *Œnothera sinuata*, *Hypoxis erecta*, butter-cups, alamander, wild daisy, a yellow wild flower, and leaves of the yellow coleus.

Class III.—In this class the materials give an extract which are red or a shade of red when acid, yellow or a shade of yellow when alkaline. All the colors are fairly sensitive, being changed by at least two drops of tenth-normal ammonia. Twenty-one of the 81 materials examined fall into this group, 11 being originally red or pink flowers, 4 orange or yellow, 5 purple or violet, 1 green (coleus leaf). The red and pink flowers were: the pink, rose (faint pink, rose, and wild rose), pink larkspur, crimson clover, phlox (faint pink, light claret, rose, scarlet, magenta), begonia (2 varieties), double oleander, a variety of *Eupharbia*, *Spensonia goligefolia rosa*, *Clerodendrum*, and *Silene Virginica*. With the exception of *Clerodendrum*, which gave a well-colored, orange-pink solution, all of the flowers above named were bleached when boiled with water, giving a colorless or faintly colored solution, which, however, became colored on the addition of acid or ammonia. Verbena flowers gave extracts, yellow with caustic soda, but green with ammonia, and the extract from sweet peas green when first made alkaline, became yellow on standing. These two are included in Class IV.

The purple or violet flowers were, the vetch, Mexican sage, heliotrope, *Clematis ochroleuca*, and *Solonum Carolinaensis*. They were bleached by the boiling. The orange or yellow flowers were orange nasturtium and canna, *Asclepias tuberosa*, yellow *Alamander vereofolia*. The yellow color of the flower was unaffected, but a colorless or faintly colored extract was formed which became colored on addition of acid or ammonia. A red-orange extract was obtained from the green part of the leaf of a red and green coleus, which was red with acid and brown-yellow with ammonia.

Class IV.—This includes those coloring-matters which are a shade of red when acid, a shade of green when alkaline. The greens are at times of a beautiful emerald color, sometimes of a yellowish tinge. Most of the colors are very sensitive to the reagents, being affected by less than 1 drop of tenth-normal ammonia.

Thirty of the materials examined fall into this class, 15 being originally a shade of red, 9 violet or purple, 3 blue, 1 lilac, 1 black (bean), 1 yellow. The flowers a shade of red were: red clover, scarlet sage, Canterbury bell, red zinna, rose geranium, crimson honeysuckle, California poppy, verbenas (faint pink and rose), sweet peas (faint pink, rose, maroon, magenta, lavender), gladiolus (rose), red cyclomen, varieties of *Bumaldae*, hibiscus, *Tephrosia* (devil's shoestring), and leaves from four varieties of coleus. With the exception of hibiscus, scarlet sage, and coleus, the extracts from these were colorless or nearly so.

The purple or violet flowers were phlox, petunia, coriopsis, verbena, sweet peas, "Jimson weed," maypop, or passion flower, *Specularia perfoliata* and *Ruellia ciliosa*.

The lilac flower was *Salvia urtica*, the blue ones were *Ageratum*, *Runella vulgaris*, and blue larkspur, the yellow one was nasturtium, and the black material, a cow-pea bean.

The colors from some of these flowers passed through several stages on the way from acidity to alkalinity. The most noteworthy are:

Specularia perfoliata: Magenta, blue, green.

Ruellia ciliata: Rose, lilac, green.

Salvia urtica: Claret, peacock blue, green.

"Jimson weed": Magenta, purple, green.

Maypop: Magenta, blue, green-blue, olive green.

Blue larkspur: Magenta, purple, blue, peacock-blue, green.

Purple petunia: Magenta, purple, blue, green.

California poppy: Magenta, purple, violet, peacock-blue, green.

Red coleus: Red, claret, violet, green.

Red and yellow coleus: Rose, brown-red, orange-red, yellow-green, olive-green.

Light red, dark red, and green coleus: Cherry, violet, brown, green-brown, dirty green.

Red and deep red coleus: Magenta, purple, blue, green.

Most of the colors above given were very bright and beautiful, and, as a rule, fairly sensitive.

The coloring-matters of the following flowers in this group

are especially sensitive: "Jimson weed," Maypop, *Salvia urtica*, black cow-pea (bean), *Ruellia ciliata*.

Class V.—This group includes substances giving colors with acid and alkali that do not come into the classes already described.

The colors are those produced by ammonia. The color, when acid, is given first, then the stages it passes through to alkaline:

Bouganvillea spectabilis (mauve): Purple, colorless.
Gloxinia hybridia (pink): Pink, purple, brownish red.
" " (purple): Magenta, purple, olive-green.
Dendrobium nobitia (purple): Pink, purple, blue, green.
Amaryllis (red): Cherry, maroon.
Salvia (red): Orange, dark red.
Cynthia (yellow): Yellow, terra-cotta.
Geranium (scarlet): Scarlet, violet.
Galardium (red): Scarlet, corn, yellow-brown.
Snapdragon (red): Red, red-brown.
Canna (red): Red, orange-brown:
Fruit:
Smilaxberries (red): Pink, violet.
Beets (red): Magenta, purple.
Strawberries: Straw, purple.
Blackberries: Rose, colorless.
Mulberries: Cherry, violet.
Brown cow-pea bean: Colorless, brown.

LABORATORY OF THE N. C. COLLEGE
OF A. and M. ARTS, June, 1900.

A NEW SYNTHESIS OF SECONDARY AMINES.

BY ALFRED TINGLE.

Theoretical.

It has been already shown[1] that when methylic salicylate is boiled with aniline the chief products are methylaniline and phenol. In the present research an attempt has been made to extend this reaction to the production of other diamines. A study has been made of the action of ethylic and isoamylic

[1] This JOURNAL, **24**, 57.

salicylates on aniline and of methylic salicylate on ammonia.

When ethylic salicylate and aniline are boiled together for seven hours the reaction between them is extremely slight, and most of the ester can be recovered unchanged. A small quantity of salicylanilide is formed, with a varying amount of phenol, and a base, the hydrochloride of which melts at 172°–174°. The quantity of the latter obtained was too small for purification and analysis, even when 16 grams of ester were used in its preparation, but its melting-point is in agreement with that given by Reynolds[1] for ethylaniline hydrochloride.

Under like circumstances, isoamylic salicylate and aniline react to about the same extent. In this case no salicylanilide appears to be formed at all; 20 grams of isoamylic salicylate gave only 0.3 gram of phenol; the hydrochloride of a base, probably isoamylaniline, was obtained, but not in quantity sufficient for analysis. It melted at 181°–182°, was very soluble in water, and did not form a stable chloroplatinate. This latter fact is in accordance with the statement of A. W. Hofmann,[2] who first described isoamylaniline and its hydrochloride. Unfortunately, neither he nor Spady,[3] who subsequently obtained them, have left any record of the melting-point of the latter. Limpricht[4] has shown that alcoholic ammonia reacts with methylic salicylate, giving salicylamide. In the present research, gaseous ammonia was passed into boiling methylic salicylate, and the gaseous reaction-products were absorbed in water. Under these circumstances dimethylamine is formed. Its chlorplatinate has been prepared and analyzed. Its formation does not seem to be accompanied by that of any mono- or trimethylamine.

The large amount of unchanged ammonia which accompanies the amine constitutes the chief difficulty which has to be overcome in its preparation by this method. The reaction between methylic salicylate and ammonia gas is not so simple as that between alkyl salicylates and aniline. The products formed simultaneously with dimethylamine, and which remain dissolved in the unchanged methylic salicylate, have not yet been fully

[1] J. Chem. Soc. (London), 1892, 455.
[2] Ann. Chem. (Liebig), **74**, 153.
[3] Ber. d. chem. Ges., **18**, 3377.
[4] Ann. Chem. (Liebig), **98**, 258.

investigated, but it would appear that phenol is not among them.

The present investigation, as far as it has been carried, shows, therefore, that alkyl salicylates are capable of introducing their alkyl group into the aniline molecule, forming monalkylated anilines. This reaction takes place with difficulty when the alkyl group is other than methyl. Methylic salicylate is also capable of introducing two methyl groups into ammonia, forming dimethylamine. The formation of primary or tertiary amines by this reaction has not been observed, and it is believed that its chief practical value, if it should prove to possess any, will depend on this circumstance.

It appears that the only means previously recorded for the preparation of isoamylic salicylate is that of Drion,[1] which depends on the interaction of salicyl chloride and amylic alcohol. The writer obtained an excellent yield of ester by using an extension of Fischer's method, boiling together amylic alcohol, salicylic acid, and a small quantity of concentrated sulphuric acid.

Practical.

Preparation of Isoamylic Salicylate.—To obtain the isoamylic salicylate employed in these experiments, an extension of Fischer's esterification method was used: 50 grams of salicylic acid, 100 cc. of commercial amylic alcohol, and 15 cc. of concentrated sulphuric acid were boiled together for three hours. When cold, the product was washed with a solution of sodium carbonate and extracted with ether. The ethereal layer, after being dried over calcium chloride, was submitted to a single fractional distillation. The fraction passing over between 265° and 275° was accepted as isoamylic salicylate, the boiling-point of which is stated by Drion[2] to be 270°. The yield of ester so obtained was 59.6 grams. From the alkaline washings 6.6 grams of salicylic acid were recovered.

Action of Ethylic Salicylate on Aniline.—16.6 grams (1 mol.) of ethylic salicylate, and 27.9 grams (3 mols.) of aniline were boiled together in a Kjeldahl flask for more than seven hours.

[1] Compt. rend., 39, 122; Ann. Chem. (Liebig), 92, 313.
[2] *Loc. cit.*

The mixture was then transferred to a Würtz flask and distilled ; the greater portion of the liquid passed over between 185° and 215°. The small tarry residue was crystallized from dilute alcohol. It then melted at 126°, and was identified as salicylanilide.

The distillate was acidified with dilute hydrochloric acid and extracted with ether. The extract consisted almost entirely of unchanged ethylic salicylate, but in most experiments traces of phenol were also detected.

The free bases were subsequently obtained by the addition of alkali to their acid solution, and extraction with ether. Fractional distillation of the mixture gave a few drops of oil boiling above 190°. Its sulphate was readily soluble in water. Its hydrochloride was still more so, and melted at 172°–174°. The quantity obtained was entirely insufficient for analysis, but there can be little doubt that it is identical with ethylaniline hydrochloride, the melting-point of which is given by Reynolds[1] as 172°–173°.

Action of Isoamylic Salicylate on Aniline.—20.9 grams (1 mol.) of isoamylic salicylate and 27.9 grams (3 mols.) of aniline were boiled together in a Kjeldahl flask for six hours. On distilling the mixture two fractions were obtained boiling respectively above and below 200°. No salicylanilide could be detected in the tarry residue. The more volatile portion of the distillate was shaken with a solution of potassium hydroxide and the excess of aniline extracted with ether. On subsequently acidifying the alkaline liquid 0.3 gram of phenol was obtained. This was identified by its smell, and by the formation of tribromphenol.

The less volatile fraction resulting from the above distillation was treated with dilute sulphuric acid, and unchanged isoamylic salicylate was extracted with ether. The bases present were obtained by neutralization of the acid solution and extraction with ether. They were afterwards dissolved in aqueous hydrochloric acid. On evaporating this solution, crystals separated, melting at 194°–195°. These were identified as aniline hydrochloride (m. p. 195°). The mother-liquor from the crystals, on further evaporation, gave a crop of much

[1] *Loc. cit.*

smaller crystals, melting definitely at 181°–182°. It seems probable, considering the manner of their formation, that these are isoamylaniline hydrochloride. No record appears to have been made of the melting-point of this substance, which has been described by A. W. Hofmann[1] and by J. Spady.[2] It was not found possible to prepare the chlorplatinate in a pure condition (which so far agrees with Hofmann's statements), and the quantity obtained was so small as to render analysis by any other method impossible.

Action of Ammonia on Methylic Salicylate.—Dry ammonia gas was conducted into a flask containing boiling methylic salicylate. The tube delivering the ammonia was made to dip far below the surface of the liquid. A second tube, high in the neck of the flask, allowed the gaseous products to escape, and led them into an absorption flask containing water. Provided that a long-necked flask was used, it was found that a condenser was not necessary to prevent the carrying over of ester. The action was allowed to proceed for thirty minutes in the first experiment, but in subsequent ones this was increased to three hours. At the end of this time the contents of the absorption flask were neutralized with hydrochloric acid, and the resulting solution was evaporated to dryness. The residue was extracted with boiling absolute alcohol, and the solution so obtained was evaporated in its turn, the resulting solid being freed from any remaining ammonium chloride by a second extraction. To this alcoholic solution platinic chloride was added; the yellowish precipitate which at once formed was filtered off, dried at 100°, and analyzed.

Two determinations, from separate preparations, were made:

I. 0.0326 gram of chlorplatinate gave 0.0139 gram of platinum on ignition, or 42.63 per cent.

II. 0.1073 gram of chlorplatinate gave 0.0464 gram of platinum on ignition, or 43.24 per cent.

Calculated for $[NH_2(CH_3)_2]_2PtCl_6$ = 42.99 per cent Pt.

The yield of dimethylamine is small in proportion to the quantity of ammonia which passes over. The substances simultaneously formed and retained in solution by the excess of

[1] *Loc. cit.* [2] *Loc. cit.*

methylic salicylate have not yet been thoroughly investigated. Among them a small quantity of salicylamide has been found and identified by the fact that it melted at 137°. No phenol has been detected. The writer proposes to continue and extend this research.

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NOTE.

On Higher Superoxides of Hydrogen.

About three years ago A. Bach[1] noted that the oxidation-products of nascent hydrogen, produced from palladium hydride, oxidize indigo solutions more rapidly than hydrogen peroxide does. This observation led him to the conclusion that during the slow oxidation of hydrogen a higher peroxide of hydrogen is formed; namely, hydrogen tetroxide, H_2O_4, analogous to potassium tetroxide.

In a recent paper Bach[2] has endeavored to determine experimentally whether higher superoxides of hydrogen exist.

The formation of hydrogen trioxide, H_2O_3, had already been suspected by Berthelot.[3] He noticed that, when potassium permanganate is titrated with hydrogen peroxide at low temperatures, the permanganate is decolorized without the liberation of oxygen. He concluded that this is due to the formation of a compound, H_2O_3, which is stable only at low temperatures.

The apparatus used by Bach in his work[4] is described by him in detail. It consists essentially of a burette so connected with a gas measuring-tube, that the solution under investigation can be titrated with potassium permanganate at the same time that the oxygen liberated can be collected and measured.

The author's criterion for the presence of a higher superoxide of hydrogen, is the amount of oxygen liberated when the solution is titrated with potassium permanganate. In accordance with the equation,

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2,$$

one molecule of oxygen is liberated for each molecule of hydrogen peroxide present, while, according to the equation,

[1] Compt. rend., 1897, 951.
[2] Ber. d. chem. Ges., **33**, 1506.
[3] Ann. chim. phys., 1880, 146.
[4] *Loc. cit.*

$$2KMnO_4 + 5H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10O_2,$$

each molecule of hydrogen tetroxide requires just as much potassium permanganate as a molecule of hydrogen peroxide, and twice as much oxygen is liberated.

In his experiments, Bach used the oxidation-products of hydrogen in the nascent state, hydrogen superoxide from potassium tetroxide, hydrogen superoxide from sodium dioxide and "Caro's acid." The last was prepared by treating a well cooled weak solution of hydrogen peroxide with concentrated sulphuric acid. If we represent by 1 the amount of oxygen liberated by hydrogen peroxide and potassium permanganate, then the amounts of oxygen liberated by corresponding amounts of the superoxides of hydrogen obtained from different sources are as follows :

Hydrogen peroxide.	Oxidation-products of hydrogen in the nascent state.	Hydrogen superoxide from sodium dioxide.	Hydrogen superoxide from potassium tetroxide.	"Caro's acid."
1	1.07	1.17	1.28	1.65

These results show that the solutions of the superoxides in question contained higher superoxides, which might be either hydrogen trioxide or hydrogen tetroxide. The author concludes from various considerations that hydrogen trioxide was not present.

From these experiments, then, it would seem that hydrogen tetroxide is capable of existence. The series of oxygen compounds of hydrogen hence consists of the following members : H_2O, H_2O_2, H_2O_3, H_2O_4. To this series should belong the suboxide H_4O. If Brühl's hypothesis of the tetravalence of oxygen is correct, this suboxide ought to be formed by the addition of hydrogen to water. Up to the present, however, all efforts to prepare it have failed. C. E. C.

CORRESPONDENCE.

To the Editor :

The review of Arey's "Elementary Chemistry" which appeared in the April number of your Journal was written by one who so evidently fails to understand the book, or who holds opinions on the principles and methods of pedagogy which differ so widely from those of our best writers on the subject, that I desire that the other side of the case be submitted to your readers.

In his opening paragraph the reviewer states that the plan

of the book assumes that the pupil at the outset is capable of making good observations, an inference which is clearly illogical. The only assumption which a book intended to cultivate the observation makes, is that the first exercises in the book are adapted to the natural powers of the student. Continuing this topic the reviewer says, " This does not accord with experience." And here he makes a serious omission in that he fails to state whose experience he refers to. Most teachers have learned that children are keen observers, and that it is very easy to guide their observations by simple questions. It is only after the functional activity of this faculty has been atrophied by some so-called teacher who would reprimand a pupil for " venturing to express an opinion " as the reviewer says should be done, that the natural powers of observation fail to respond.

In the same paragraph the reviewer remarks, " It would certainly be interesting to read the note-books of pupils who without directions from the teacher should record the results of their first observations on chemical substances." In reply I beg to say that I think it would be interesting, and instructive also, to the reviewer.

I do not mean to say that it would be considered sound pedagogics to-day to give a beginner a complex organic substance and to require him to study it until he has learned all that is known about it; yet this was Agassiz' method, and where is there a greater teacher than he?

The modern teacher recognizes the soundness of Agassiz' method but saves time by arranging a course which, requiring at the outset only the most apparent observations and the most obvious inferences, gradually increases in difficulty of observation and in disciplinary value. He has found that the pupil's work and his thinking are best controlled by supplying directions for his experiments with questions which call for definite observations and inferences, including an occasional question which he cannot answer fully, to show him his limitations and to give him zest for further study.

The reviewer designates as " extremely dangerous " the experiment of exploding a mixture of potassium chlorate and sulphur and says that he shudders to think what the results would be if the experiment was performed by an inexperienced person. It is remarkable that after an honorable experience in the principal elementary chemistries of more than fifty years, this experiment should run amuck in this way. The writer has performed it regularly in his classes for twenty years, and having never had an accident, naturally wonders what manner of *pas de seul* the reviewer would execute if he should some-

time contemplate the results of the more dangerous experiment in which phosphorus is substituted for the sulphur of the above experiment; and yet the reviewer and other persons, often inexperienced, perform the latter experiment every time they strike a parlor match.

Now I am willing to admit that if large quantities of sulphur and potassium chlorate should be used, and if the experimenter chanced to secure a sufficiently intimate mixture of the two substances before any of it was exploded, the results might be serious, but the experiment is to be performed by the instructor, and from a personal acquaintance with the majority of the instructors of chemistry in New York State I can assure him that not one of them needs caution to use small quantities in such an experiment. However, fearing that perhaps the book might possibly fall into the hands of teachers who do need such caution, the author inserted a scare line in the teacher's handbook which accompanies the "Elementary Chemistry."

The next boomerang hurled by the reviewer has the following form: "On page 5 are found directions for an experiment which is not clear, though it sounds learned. The pupil is directed to weigh a quantity of sulphuric acid and a solution of calcium chlorid; then pour them together and weigh them again. The pupil is then asked: 'Does chemical action change the total quantity of matter in existence? Was the total quantity of sulphuric acid in the world increased or diminished by the above experiment? How was the total quantity of calcium chlorid affected?' As a matter of fact, the total quantity of sulphuric acid in the world is diminished by such an experiment, but the pupil cannot possibly know this unless told."(!)

This experiment is preceded by several experiments illustrating chemical change, in the last of which the student proves that in a given chemical change the factors have disappeared and an entirely distinct substance has been formed; with this in view they are fully able to answer the question which the reviewer says they could not possibly answer; in fact, in my last class, 31 of the 32 pupils did answer it without assistance.

The rest of the review consists of inferences concerning the personality of the writer, which are as uncalled for as they are unwarranted. To sum up: The reviewer writes from the standpoint of one who believes that the object of teaching chemistry is to make chemists of the pupils, whereas the book under review treats chemistry as a disciplinary subject.

ALBERT L. AREY.